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A diverse structural behaviour of boronated *ortho*-phthalaldehydes: A crystal structure of 1,3-dihydro-1,3-dihydroxy-4-formylbenzo[c][2,1]oxaborole

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Abstract

Two isomeric boronated *ortho*-phthalaldehydes 3- and 4-$[B(OH)_2]$-1,2-$C_6H_3(CHO)_2$ have been prepared and their specific behavior in solution under various conditions has been investigated using NMR spectroscopy. The former compound undergoes a ring-chain tautomeric rearrangement to form a cyclic structure of 1,3-dihydro-1,3-dihydroxy-4-formylbenzo[c][2,1]oxaborole predominating in acetone-d_6 solution and characterized by X-ray diffraction.

Keywords: *ortho*-Phthalaldehyde (OPA); Arylboronic acids; Ring-chain tautomerism; Benzaldehydes

1. Introduction

ortho-Phthalaldehyde (OPA) is useful in syntheses of various carbo- and heterocyclic systems with a fused benzene ring [1]. It also exhibits specific properties due to a proximity of formyl groups. In the presence of water it is strongly hydrated to form a cyclic hemiacetal (as a mixture of *cis* and *trans*-isomers) and a geminal diol [2]. Under alkaline conditions, it is prone to undergo an intramolecular Cannizzaro reaction to give the anion of 2-(hydroxymethyl)benzoic acid [3]. More recently, OPA has been recognized as the potent antibacterial agent acting due to the reaction with aminoacids and proteins [4]. Furthermore, the method of determination of trace amounts of aminoacids is based on their reactions with OPA and its analogues yielding fluorescent isoindoles [5]. In our contribution we report about novel boronated analogues of OPA. We demonstrate that the behaviour of *ortho*-phthalaldehyde system is strongly influenced by boronation of the aromatic ring.

2. Results and discussion

The synthesis of boronated *ortho*-phthalaldehydes is shown in Scheme 1. It involved a sequence of Br/Li exchange reactions with alternating formylation/protection and boronation/deprotection steps. The regioselective Br/Li exchange proceeds *ortho* to dimethoxymethyl group [6] and was a key step in a synthesis of 4-(dihydroxyboryl)-1,2-phthalaldehyde **4**.

According to a ^{1}H NMR analysis, **2** reveals a specific behaviour in acetone-d_6 solution. The spectrum exhibits only one strong resonance in a low-field range at 10.44 ppm, which can be assigned to the formyl hydrogen. Another characteristic singlet can be observed at 6.82 ppm. There are also minor peaks at 10.66 and 10.29 of equal intensities. In the ^{13}C NMR spectrum a number of resonances is increased indicating the existence of at least two species in solution. Strong resonances at 191.9 and 97.2 ppm indicate that a more abundant species contains one formyl group and one quaternized carbon. Based on

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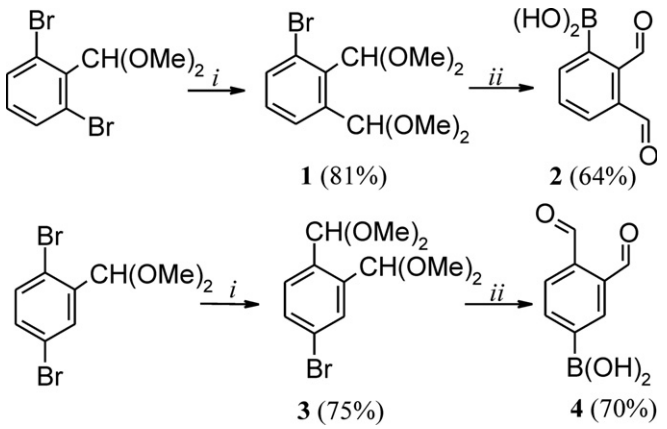
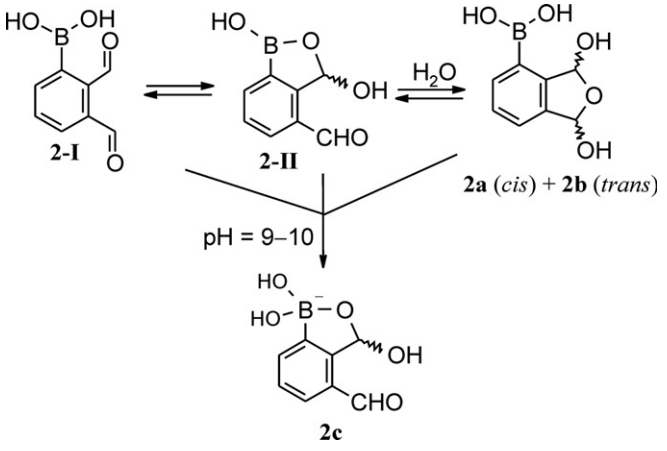


Scheme 1. The synthesis of boronated *ortho*-phthalaldehydes **2** and **4**. Reagents and conditions: (i): 1. *n*-BuLi/Et_2O (−70 °C), 2. DMF (−70 °C), 3. H_2SO_4 aq., rt, 4. MeOH, $CH(OMe)_3$, H^+ (60 °C, 1 h); (ii): 1. *n*-BuLi/THF (−70 °C), 2. $(EtO)_3B$ (−70 °C), 3. H_2SO_4 aq. (40 °C).

these observations we have formulated the structure of 1,3-dihydro-1,3-dihydroxy-4-formylbenzo[c][2,1]oxaborole **2-II** (Scheme 2) to be consistent with major resonances in ^1H and ^{13}C NMR spectra. Accordingly, smaller peaks can be assigned to a classical acyclic structure of 2,3-diformylphenylboronic acid **2-I**. Comparison of signal integration gives a cyclic to acyclic tautomer ratio of 12 at 293 K. Unlike **2**, the isomeric compound **4** exists in one typical acyclic form as evidenced by two formyl hydrogen resonances at 10.50 and 10.45 in the ^1H NMR spectrum, and corresponding signals of formyl carbons at 193.9 and 193.6 ppm in the ^{13}C NMR spectrum. Moreover, a comparison of ^{11}B NMR chemical shifts of **2** and **4** shows a downfield shift for **2**. The difference of $\delta^{11}B$ values of **2** and **4** is not large (ca. 3–4 ppm). However, both resonances are clearly distintiguishable as demonstrated by the ^{11}B NMR spectrum (64.2 MHz) of a mixed sample (see Fig. 17 in the Supplementary Material). This is in accord with general observations indicating a deshielding of boron in five-membered heterocycles containing B–O (and also B–N) bond due to an increased valence strain (reflected

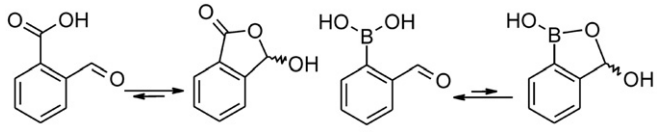


Scheme 2.

by angles at the boron atom different from 120°) and less effective π-bonding between boron and oxygen with respect to non-annelated analogues [7].

The tautomerism **2-I** ↔ **2-II** is the next example of specific processes observed in *ortho*-functionalized benzaldehydes [8] and shows a close analogy with a formation of 3-hydroxyphthalide from 2-formylbenzoic acid, which is isoelectronic with 2-formylphenylboronic acid (Scheme 3) [9]. However, it should be stressed that the presence of a formyl group in a 3-position is required for an equilibrium favouring the cyclic tautomer whereas for 2-formylphenylboronic acid only a small amount of a cyclic form (ca. 5%) was detected by ^1H NMR analysis in [D_6] acetone. Other intramolecular cyclizations leading to benzo[c][2,1]oxaboroles are more entropy-favoured due to elimination of water molecule [10,11].

The compound **2** crystallizes as a cyclic tautomer **2-II**. The molecular structure is depicted in Fig. 1. The metric features of the molecule **2-II** (Table 1) are similar to those reported for related 1,3-dihydro-1-hydroxybenzo[c][2,1]oxaborole [11], and its derivatives [12]. The 3-formyl group is nearly coplanar with the aromatic ring while the C=O bond adopts the *exo*-orientation with respect to the adjacent boraheterocycle. Apparently, the 3-formyl group impacts a specific mode of interaction between $B(OH)_2$ and an adjacent *ortho*-CHO group resulting in a destabilization of the open form **2-I**. Presumably, unfavourable steric and



Scheme 3.

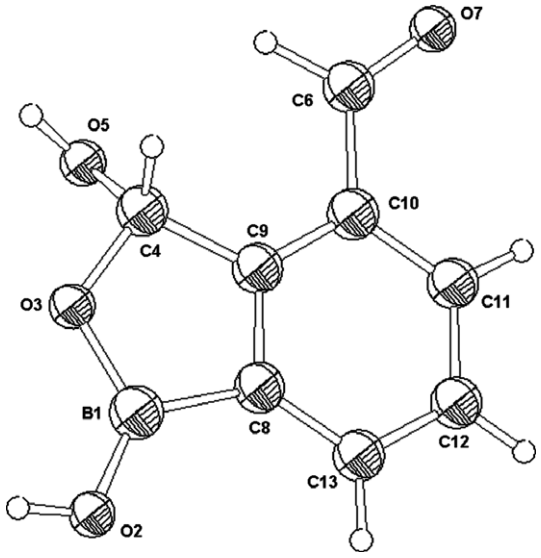


Fig. 1. The molecular structure of **2-II**. Displacement thermal ellipsoids are drawn at the 50% probability level.

dipole–dipole repulsions between adjacent formyl groups [13] in **2-I** result in a partial or even complete deconjugation between them and the phenyl ring whereas in **2-II** the formyl group is conjugated with the phenyl ring. In the related 2-formylphenylboronic acid the formyl group serves as a proton acceptor for $B(OH)_2$ group, thus producing an approximately planar seven-membered ring due to an intramolecular hydrogen bond B–OH···O=C [14]. Very recently, we have found that various 2-formylphenylboronic acids form reversibly corresponding 1,3-dihydro-1,3-dihydroxybenzo[c][2,1]oxaboroles. The cyclization is exerted mainly by the appropriate funcionalization in the 3-position of 2-formylphenylboronic acid; [15] the 3-formyl group has the strongest impact. It should be noted that the crystal structure of the cyclic tautomer of related 3-bromo-2-formylphenylboronic acid was determined but the full refinement proved difficult due to a crystal disorder [15]. Hence, the structure **2-II** is the first precise crystallographic evidence for the ring-chain tautomerism in 2-formylphenylboronic acids.

An insight into a crystal structure of **2-II** (Fig. 2) reveals a specific supramolecular assembly due to intermolecular hydrogen bonds, of which there are two types (Table 2). It can be interpreted as an array of infinite chains formed by shorter and almost linear bridges between a carbonyl oxygen and a boron-bound hydroxyl group. They are paired by cross-linking longer H bonds between a ring oxygen and a hydrogen from a carbon-bound hydroxyl group (Table 2). These weaker interactions produce another motif as a cyclic and centrosymmetric dimer. The C4 atom is asymmetric; molecules in the chain have the same configuration (i.e., *R* or *S*), whereas molecules in the parallel hydrogen-bonded chain have the opposite configuration.

Table 1
Selected bond lengths (Å) and valence angles (°) for **2-II**

Bond lengths		Bond angles	
B(1)–O(2)	1.3386(19)	O(2)–B(1)–O(3)	122.48(14)
B(1)–O(3)	1.3995(18)	O(2)–B(1)–C(8)	129.88(14)
B(1)–C(8)	1.555(2)	O(3)–B(1)–C(8)	107.64(13)
C(4)–O(3)	1.4569(17)	B(1)–O(3)–C(4)	110.84(11)
C(4)–O(5)	1.3938(17)	O(5)–C(4)–O(3)	110.18(12)
C(6)–O(7)	1.2223(18)	O(5)–C(4)–C(9)	111.00(12)
		O(3)–C(4)–C(9)	104.87(11)
		O(7)–C(6)–C(10)	124.83(14)
		C(9)–C(8)–B(1)	105.59(12)
		C(13)–C(8)–B(1)	135.44(14)
		C(8)–C(9)–C(4)	111.01(12)
		C(10)–C(9)–C(4)	126.91(13)

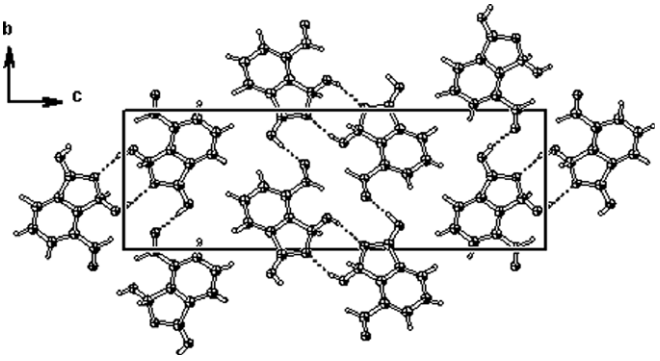


Fig. 2. The crystal packing diagram for **2-II**. Hydrogen bonds are marked by dashed lines.

Table 2
Hydrogen-bonding geometry (Å, °) for **2-II**[a]

	d(H···A)	*d*(D···A)	∠D–H···A
O(2)–H(2)···O(7)$^{\#1}$	1.863(14)	2.7185(14)	173.8(14)
O(5)–H(5)···O(3)$^{\#2}$	2.044(16)	2.8251(14)	158.7(14)

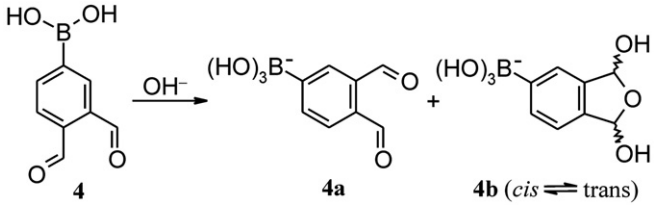
[a] Symmetry codes: $^{\#1}\,x+1,\ y-1,\ z$; $^{\#2}\,-x+1,\ -y+1,\ -z$.

We have investigated the effect of a boronic acid group on a hydration of an *ortho*-phthalaldehyde system. Upon addition of 10 wt% of D_2O to an acetone-d_6 solution of **2**, two new characteristic sets of resonances now appear in a ^1H NMR spectrum of **2**. The first one is represented by two singlets at 6.22 and 6.29 ppm of equal intensities. Based on previous conclusions [2b,13,16], we have assigned these signals to C*H*(OH) hydrogens of the *cis*-isomer of a cyclic hemiacetal **2a**. The second set of slightly less intensive signals comprises two weakly coupled doublets due to $^4J_{CH-O-CH} = 2.0$ Hz at 6.52 and 6.62 ppm. Accordingly, they can be assigned to hemiacetal protons of a *trans*-isomer **2b**. Based on integrations of aforementioned signals the ratio **2a**/**2b** is ca. 5:4. Further changes are observed in the aromatic region. The partial assignment of characteristic ^{13}C NMR resonances at 99.9 and 100.2 (**2a**), 100.8 and 101.2 (**2b**) was performed by 2D HETCOR (^1H,^{13}C) experiment. The overall degree of hydration of **2** in a dilute (ca. 0.05 M) solution in acetone-d_6/D_2O (90:10) is ca. 0.6 and decreases only slightly upon heating from 293 to 321 K. The equilibrium **2-I** ↔ **2-II** is not significantly affected by the addition of D_2O. However the ratio **2-II**/**2-I** is temperature sensitive and decreases from the value of 14 at 293 K to 9 at 321 K. Surprisingly, the compound **4** does not undergo hydration under comparable conditions as indicated by NMR spectra, where no new signals of hemiacetal hydrogen and carbon atoms could be recorded upon addition of D_2O. The ^{11}B NMR spectrum of a mixed sample containing **2** and **4** in acetone-d_6 changes significantly after addition of D_2O: the well-resolved resonance of **2-II** at 31 ppm collapses to leave only a shoulder (see Fig. 18 in the Supplementary Information), which reflects a reduced abundance of the cyclic form **2-II** under these conditions. On the contrary, the signal at 28 ppm assigned to **4** remains essentially unchanged.

We have investigated the behaviour of boronated *ortho*-phthalaldehydes **2** and **4** under moderately alkaline (0.5 M K_2CO_3/D_2O, pH 9–10) aqueous conditions. Clean ^1H and ^{13}C NMR spectra indicate that only one species is present. There are singlet proton resonances at 10.15 and 6.57 ppm, to which correspond two ^{13}C NMR signals at 202.7 and

100.6 ppm. All these data are in agreement with a structure of a cyclic boronate **2c** (Scheme 2). Importantly, there are no signals that could be assigned to anionic forms of hydrated species **2a**–**2b**. Further confirmation comes from the ^{11}B NMR spectrum, where a single resonance of a tetravalent boron species appears at 4.5 ppm. A clean formation of the analogous cyclic anionic species under moderately alkaline conditions was also observed for 3-fluoro-2-formylphenylboronic acid, which also undergoes ring-chain tautomerism [15]. In practical terms, it seems advantageous to use such conditions to determine the purity of various 2-formylphenylboronic acids by NMR as spectra should be simplified when compared to those recorded under standard conditions (i.e., without addition of base).

A different situation is observed in alkaline (pH 9–10) solution of **4** in D_2O. According to a ^{1}H NMR spectrum showing resonances of two formyl groups, a boronate anion **4a** resulting from a simple complexation of boron by hydroxide is formed (Scheme 4). However, it is accompanied by a comparable proportion of another species characterized by a broad resonance at 6.54 ppm and separate multiplets in the aromatic region. We have formulated it as a boronate anion of a cyclic hemiacetal **4b**, i.e., a hydrated form of **4a**. Assuming the hydration of benzaldehydes being generally favoured by electron-withdrawing groups [17], we were again confused as we initially expected that the hydration of **4a** should not occur due to an increased charge density within the aromatic system upon boron complexation. The hemiacetal hydrogen as well as aromatic and hemiacetal carbon resonances of **4b** are strongly broadened. It is indicative of *cis* ↔ *trans* interconversion occuring within the heterocyclic system quite rapidly on the ^{1}H NMR time-scale [2b]. In the ^{11}B NMR spectrum, a signal with a maximum at 0 ppm, i.e., in the range typical of metal aryl(alkoxy)borates [18], has a shoulder at ca. 1 ppm indicating a detectable difference of ^{11}B NMR chemical shifts of **4a** and **4b**. This small difference cannot be meaningfully interpreted; it is only our hypothesis that it may reflect a change of the electronic character of the phthalaldehyde system upon hydration, which in turn slightly affects boron chemical shift. Notably, the boron atom in the cyclic borate anion **2c** exhibits a low field shift (ca. 3–4 ppm) with respect to those in **4a**–**4b**; this effect is comparable to that observed for neutral forms **2** and **4**. Unfortunately, the limited number of ^{11}B NMR data for related aryl(alkoxy)borates precludes a detailed discussion of this point. However, it is clear that a different interpretation should be formulated to account for the difference of δ^{11}B values for tetravalent borates as unlike their tetravalent precursors π-bonding is lacking; moreover, the ring-strain in **2-II** is apparently reduced or removed due to rehybridization.



Scheme 4.

3. Conclusions

In conclusion, the boronated *ortho*-phthalaldehydes exhibit interesting and diverse properties. The substituent-dependent tautomeric cyclization is a general structural feature of functionalized *ortho*-formylphenylboronic acids, disturbing their analysis and purity determination. However, this complication can simply be overcome as under moderately alkaline conditions only one type of anionic cyclic boronate is formed. The hydration of phthalaldehyde system in **2** and **4** is strongly dependent on the position and charge of boron-containing moiety. It is intriguing that these results are not in line with previous findings showing that the hydration is stronger for more electron-deficient benzaldehyde systems. Last but not least, there is an open field for research focused on the practical use of boronated analogues of OPA, e.g., as molecular recognition reagents. Recently, 1,3-dihydro-1-hydroxybenzo[c][2,1]oxaborole has been recognized to show a strong binding to glucose and methyl α-D-glucopyranoside [19]. It also proved useful in the Fourier transform ion cyclotron resonance mass spectrometry analysis of products of formose reaction [20]. We hope that the closely related species **2-II** could also be capable of binding to carbohydrates; we are planning to undertake a work in this field. There is also a wide potential for the use of **2** and **4** as Suzuki coupling partners in the construction of various systems containing the OPA building block, e.g., for a potential application as aminoacid receptors [5]. Finally, considering the microbiological activity of OPA [4] as well as arylboronic acids [21] and specifically benzo[c][2,1]oxaboroles [22], the use of boronated OPAs in this area can be anticipated as a promising task.

4. Experimental

All reactions were carried out under an argon atmosphere. Solvents were stored over sodium wire before use. *n*-Butyllithium (10 M solution in hexanes), triethyl borate, *N*,*N*-dimethylformamide (DMF), and trimethyl orthoformate were used as received. 1,3-dibromo-2-(dimethoxymethyl)benzene [15] and 1,4-dibromo-2-(dimethoxymethyl) benzene [6] have been prepared according to the literature procedures.

The ^{11}B NMR chemical shifts were given relative to $F_3B \cdot Et_2O$. The ^{13}C NMR chemical shifts for samples dissolved in K_2CO_3/D_2O were calibrated using the value of 168.3 ppm referenced for K_2CO_3 [23].

4.1. 1,2-Bis(dimethoxymethyl)-3-bromobenzene (**1**)

The solution of 1,3-dibromo-2-(dimethoxymethyl)benzene (9.3 g, 30 mmol) in ether (30 mL) was addded to the solution of BuLi (10 M, 3 mL, 30 mmol) in ether (50 mL) at −78 °C. After 15 min stirring DMF (2.9 g, 40 mmol) was added at −78 °C. The mixture was stirred for 30 min, then it was allowed to warm to ca. −50 °C followed by hydrolysis with 2 M aq. HCl. The organic layer was separated followed by evaporation of the solvent under reduced pressure. To an oily residue, trimethyl orthoformate (6.4 g, 60 mmol), methanol (10 mL) and a drop of conc. H_2SO_4 were added. The mixture was heated for 1 h at reflux and neutralized with sodium methoxide. Volatiles were removed under reduced pressure and a residue was distilled in vacuo to give the title compound as colorless oil (7.3 g, 81%), b.p. 125–130 °C (1 Torr). IR (film) ν/cm^{-1} 2932, 1448, 1372, 1212, 1072, 968; ^1H NMR ($CDCl_3$, 400 MHz) δ: 7.67 (1H, dd, J 8.0, 1.5 Hz, Ph), 7.53 (1H, dd, J 8.0, 1.5 Hz, Ph), 7.22 (1H, td, J 8.0, 0.5 Hz, Ph), 5.96 (1H, s, C*H*(OMe)$_2$), 5.86 (1H, d, C*H*(OMe)$_2$), 3.46 (6H, s, OMe), 3.41 (6H, s, OMe); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ: 141.1, 134.5, 133.0, 130.3, 127.0, 123.4, 106.7, 101.7, 55.6, 55.3. Anal. Calc. for $C_{12}H_{17}BrO_4$ (305): C, 47.23; H 5.62. Found: C, 47.57; H 5.51%.

4.2. 1,2-Bis(dimethoxymethyl)-4-bromobenzene (**3**)

This compound was prepared starting with 1,4-dibromo-2-(dimethoxymethyl)benzene (9.3 g, 30 mmol) as described for **1**. Colorless oil (6.80 g, 75%), b.p. 128–132 °C (1 Torr); IR (film) ν/cm^{-1} 2936, 1356, 1192, 1052, 984; ^1H NMR ($CDCl_3$, 400 MHz) δ: 7.76 (1H d, J 1.5 Hz, Ph), 7.49–7.44 (2H, m, Ph), 5.65 (1H, s, C*H*(OMe)$_2$), 5.63 (1H, s, C*H*(OMe)$_2$), 3.31 (6H, s, OMe) and 3.30 (6H, s, OMe); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ: 137.8, 134.7, 131.2, 129.8, 128.6, 122.6, 100.2, 99.8, 53.15, 53.14. Anal. Calc. for $C_{12}H_{17}BrO_4$ (305): C, 47.23; H 5.62. Found: C, 47.43; H 5.40%.

4.3. 3-(Dihydroxyboryl)-1,2-phthalaldehyde (**2**)

A solution of **1** (6.1 g, 20 mmol) in ether (20 mL) was added dropwise to the solution of BuLi (10 M, 2 mL, 20 mmol) in ether (30 mL) at −75 °C. After 15 min stirring $B(OEt)_3$ (3.2 g, 22 mmol) was added at −75 °C. The mixture was stirred for 30 min, then it was allowed to warm to ca. −50 °C followed by hydrolysis with 2 M aq. HCl. The organic layer was separated followed by evaporation of the solvent under reduced pressure. Water (10 mL) and a drop of conc. aq. HCl were added and a mixture was heated shortly to ca. 60 °C to cleave the acetal protection followed by removal of methanol in vacuo. A crude solid product was filtered and washed with cold water (2 × 5 mL) and toluene (2 × 5 mL) to give the title compound (2.26 g, 64%), m.p. 149–151 °C (dec); IR (KBr) ν/cm^{-1} 3428, 3276, 1680, 1468, 964, 704; ^1H NMR ($(CD_3)_2CO$, 400 MHz) δ: 10.68 (1H, s, **2-I**), 10.44 (1H, s, **2-II**), 10.33 (1H, s, **2-I**), 7.98-7.95 (2H, m, **2-II**), 7.78 (1H, t, J 7.5 Hz, **2-I**), 7.61 (1H, t, J 7.5 Hz, **2-II**), 6.82 (1H, s, **2-II**), 3.07 (broad, OH); ^{11}B NMR ($(CD_3)_2CO$, 64.2 MHz) δ: 32.0; ^{13}C NMR ($(CD_3)_2CO$, 100.6 MHz) δ: 191.5, 156.9, 138.5, 136.75, 136.67, 136.5, 132.2, 130.9, 130.2, 129.5, 125.7, 97.5. Anal. Calc. for $C_8H_7BO_4$ (178): C, 54.00; H, 3.97. Found: C, 53.96; H, 4.03%.

4.4. 4-(Dihydroxyboryl)-1,2-phthalaldehyde (**4**)

This compound was prepared as described for **2** starting with **3** (6.1 g, 20 mmol); yield 2.5 g (70%), m.p. 222–225 °C (dec). IR (KBr) ν/cm^{-1} 3420, 1690, 1668, 1336, 1208, 1052, 644; ^1H NMR ($(CD_3)_2CO$, 400 MHz) δ: 10.56 (1H, s, CHO), 10.51 (1H s, CHO), 8.44 (1H, d, J 1.0 Hz, Ph), 8.28 (1H, dd, J 7.5 and 1.0 Hz, Ph), 7.97 (1H, d, J 7.5 Hz, Ph), 7.86 (s, $B(OH)_2$) and 3.15 (s, $B(OH)_2$); ^{11}B NMR ($(CD_3)_2CO$, 64.2 MHz) δ: 28.0; ^{13}C NMR ($(CD_3)_2CO$, 100.6 MHz) δ: 193.9, 193.6, 140.0, 138.6, 137.3, 136.5, 130.1. Anal. Calc. for $C_8H_7BO_4$ (178): C, 54.00; H, 3.97. Found: C, 53.81; H, 4.14%.

Crystal structure determination of **2-II**.

Details regarding crystal structure determination of **2-II** are given in Table 3.

Single crystals of **2-II** were grown by slow evaporation of a solution of **2** (ca. 0.2 g) in wet ethyl acetate

Table 3
Crystal data, data collection and refinement parameters for compound **2-II**

Empirical formula	$C_8H_7BO_4$
Formula weight	177.95
Radiation	Mo Kα ($\lambda = 0.71073$ Å)
Temperature (K)	100(2)
Crystal system	Monoclinic
Space group	$P2(1)/n$
Z (Z')	4
a (Å)	3.8941(2)
b (Å)	8.0550(5)
c (Å)	24.4138(14)
α (°)	90
β (°)	94.507(3)
γ(°)	90
Volume (Å^3)	763.42(8)
Absorption coefficient (mm^{-1})	0.122
θ Range (data collection)	2.66–28.68
Index range	$4 \leqslant h \leqslant 5$, $-10 \leqslant k \leqslant 10$, $-31 \leqslant l \leqslant 32$
Reflections collected	7222
Unique reflections (R_{int})	1901 (0.0324)
Data/restraints/parameters	1901/0/145
Goodness-of-fit on F^2 [a]	0.832
Final R indices ($I > 2\sigma(I)$) [b]	$R_1 = 0.0309$, $wR_2 = 0.0487$
R indices (all data) [b]	$R_1 = 0.0538$, $wR_2 = 0.0509$
Largest difference in peak and hole (eÅ^{-3})	+0.195 and −0.197

[a] Goodness of fit $S = \{[w(F_o^2 - F_c^2)^2]/(n-p)\}^{1/2}$ where n is the number of reflections and p is the total number of parameters refined.

[b] $R_1 = \sum||F_o| - |F_c||/\sum|F_c|$, $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

(ca. 15 mL), which was obtained by the addition of a few drops of water to a reagent grade solvent [24]. The use of dry EtOAc and other solvents (acetone, acetone + water) did not afford crystals having a sufficient quality. All measurements were performed on a KM4CCD κ-axis diffractometer with graphite-monochromated Mo Kα radiation. The crystal was positioned at 62 mm from the CCD camera. 1500 frames were measured at 0.4° intervals with a counting time of 18 s. The data were corrected for Lorentz and polarization effects. Empirical correction for absorption was applied. Data reduction and analysis were carried out with the Oxford Diffraction programs CrysAlis CCD and CrysAlis RED, Version 1.171.28cycle2 beta.

The structure **2-II** was solved by direct methods [25] and refined using SHELXL97. The refinement was based on F^2 for all reflections except those with very negative F^2. Weighted R factors wR and all goodness-of-fit S values are based on F^2. Conventional R factors are based on F with F set to zero for negative F^2. The $F_o^2 > 2\sum(F_o^2)$ criterion was used only for calculating R factors and is not relevant to the choice of reflections for the refinement. The R factors based on F^2 are about twice as large as those based on F. All hydrogen atoms were located geometrically and their positions were refined. Temperature factors of three hydrogen atoms were not refined. Scattering factors were taken from Tables 6.1.1.4 and 4.2.4.2 [26]. The crystal was a pseudo-merohedral twin with a refined component occupancy of 42.51(9)%. The twinning is due to the rotation around the [1 0 0] direction by the angle of 180°, which is represented by the matrix $\{1\,0\,0\,0\,\bar{1}\,0\,\bar{1}\,0\,\bar{1}\}$. Another possibility involves the rotation around the [1 0 2] direction by the angle of 180°, which is represented by the matrix $\{\bar{1}\,0\,0\,0\,\bar{1}\,0\,1\,0\,1\}$.

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Appendix A. Supplementary material

CCDC 616906 contains the supplementary crystallographic data for **2-II**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2007.03.001.

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