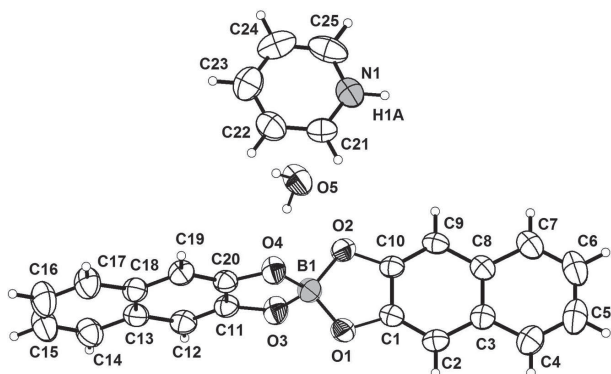


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# Crystal structure of pyridinium bis(naphthalene-2,3-diolato- $\kappa^2O,O'$ )borate monohydrate, $C_{25}H_{20}BNO_5$



**Table 1:** Data collection and handling.

Crystal:	Colourless prism
Size:	0.50 × 0.40 × 0.12 mm
Wavelength:	Mo K $\alpha$ radiation (0.71073 Å)
$\mu$ :	0.9 cm <sup>-1</sup>
Diffractometer, scan mode:	Xcalibur, $\omega$ -scans
2 $\theta$ <sub>max</sub> , completeness:	52.8°, >99%
$N(hkl)$ <sub>measured</sub> , $N(hkl)$ <sub>unique</sub> , $R_{int}$ :	7281, 4305, 0.014
Criterion for $I_{obs}$ , $N(hkl)$ <sub>gt</sub> :	$I_{obs} > 2 \sigma(I_{obs})$ , 3102
$N(param)$ <sub>refined</sub> :	299
Programs:	CrysAlis [20], SHELX [21]

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## Abstract

$C_{25}H_{20}BNO_5$ , triclinic,  $P\bar{1}$  (no. 2),  $a = 7.0868(6)$  Å,  $b = 10.3522(6)$  Å,  $c = 15.3140(10)$  Å,  $\alpha = 74.088(7)^\circ$ ,  $\beta = 89.996(7)^\circ$ ,  $\gamma = 79.190(1)^\circ$ ,  $V = 1059.71(13)$  Å<sup>3</sup>,  $Z = 2$ ,  $R_{gt}(F) = 0.0445$ ,  $wR_{ref}(F^2) = 0.1105$ ,  $T = 298$  K.

CCDC no.: 1488929

The asymmetric unit of the title crystal structure is shown in the figure. Tables 1 and 2 contain details of the measurement method and a list of the atoms including atomic coordinates and displacement parameters.

## Source of material

A water solution (5 mL) of  $B(OH)_3$  (124 mg, 2.00 mmol,) was carefully added to a stirred ethanole (10 mL) solution of 2,3-naphthalenediol (673 mg, 4.2 mmol) at ambient temperature.

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The reaction mixture was stirred vigorously at 338 K for 30 min. The dropwise addition of pyridine (0.5 mL, 6.2 mmol) resulted in an immediate formation of a precipitate. A light pink coloured product was obtained after 40 min of stirring. The resulting solid was dissolved in the mixture of acetone/DMF (10 mL; 1:1) and allowed to stand at room temperature for a couple of days, thereupon transparent and fine crystals were harvested. Yield: (0.61 g, 70%) (based on  $B(OH)_3$ ); Elemental analysis: (Found): C 69.57, H 4.78, N 3.37%. Calculated for  $C_{25}H_{20}O_5NB$ : C 70.61, H 4.74, N 3.29%. <sup>1</sup>H-NMR ( $d^6$ -DMSO- $CDCl_3$ , 298 K, TMS):  $\delta$  (p.p.m.): 6.70 (m, 4H), 6.97 (m, 4H), 7.37 (m, 4H), 7.76 (m, 2H, pyridinium), 8.27 (m, 2H, pyridinium), 8.65 (m, 1H, pyridinium).

## Experimental details

The H atoms of the water molecule were located in Fourier difference maps and refined freely. The remaining H atoms were positioned geometrically ( $C-H = 0.96-0.97$  Å) and refined using a riding model with  $U_{iso}(H) = 1.2$  or  $1.5U_{eq}(C)$ .

## Discussion

In recent years, attentions have been particularly paid to compounds containing borate groups on account of the fact that they possess extensive use as synthons in organic synthesis, especially in Suzuki cross coupling reactions [1]. Certain boron-containing species such as organoboronic acids  $[RB(OH)_2]$  or boronate esters  $[RB(OR')_2]$  are exceedingly alluring for these carbon–carbon bond forming reactions as

**Table 2:** Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å<sup>2</sup>).

Atom	x	y	z	U <sub>iso</sub> <sup>*</sup> /U <sub>eq</sub>
C1	0.1529(2)	0.18915(15)	-0.04570(11)	0.0409(4)
C2	0.1050(2)	0.17895(16)	-0.12874(12)	0.0468(4)
H2	0.0982	0.0944	-0.1373	0.056*
C3	0.0654(2)	0.29984(17)	-0.20252(11)	0.0457(4)
C4	0.0173(3)	0.2979(2)	-0.29141(13)	0.0628(5)
H4	0.0090	0.2148	-0.3021	0.075*
C5	-0.0174(3)	0.4141(3)	-0.36221(14)	0.0761(6)
H5	-0.0480	0.4096	-0.4202	0.091*
C6	-0.0069(3)	0.5396(2)	-0.34768(14)	0.0731(6)
H6	-0.0295	0.6188	-0.3962	0.088*
C7	0.0361(3)	0.54693(19)	-0.26290(13)	0.0602(5)
H7	0.0410	0.6317	-0.2541	0.072*
C8	0.0738(2)	0.42871(16)	-0.18787(11)	0.0453(4)
C9	0.1213(2)	0.43532(16)	-0.09975(12)	0.0454(4)
H9	0.1257	0.5188	-0.0889	0.054*
C10	0.1603(2)	0.31739(15)	-0.03158(11)	0.0408(4)
C11	0.1930(2)	0.05650(16)	0.25597(11)	0.0439(4)
C12	0.1266(2)	0.00386(17)	0.33792(12)	0.0488(4)
H12	-0.0048	0.0180	0.3465	0.059*
C13	0.2607(2)	-0.07369(16)	0.41109(12)	0.0477(4)
C14	0.2017(3)	-0.1357(2)	0.49793(13)	0.0623(5)
H14	0.0710	-0.1272	0.5078	0.075*
C15	0.3318(3)	-0.2079(2)	0.56764(15)	0.0760(6)
H15	0.2893	-0.2471	0.6245	0.091*
C16	0.5275(3)	-0.2232(2)	0.55426(15)	0.0787(6)
H16	0.6159	-0.2719	0.6023	0.094*
C17	0.5899(3)	-0.1674(2)	0.47154(13)	0.0652(5)
H17	0.7214	-0.1797	0.4633	0.078*
C18	0.4607(2)	-0.09099(16)	0.39731(12)	0.0481(4)
C19	0.5243(2)	-0.03233(17)	0.31039(12)	0.0489(4)
H19	0.6550	-0.0419	0.3004	0.059*
C20	0.3919(2)	0.03778(16)	0.24223(11)	0.0439(4)
C21	0.3748(3)	0.5365(2)	0.11457(14)	0.0594(5)
H21	0.3493	0.4811	0.0792	0.071*
C22	0.4305(3)	0.4804(2)	0.20310(15)	0.0677(5)
H22	0.4442	0.3864	0.2286	0.081*
C23	0.4661(3)	0.5600(3)	0.25446(16)	0.0748(6)
H23	0.5026	0.5218	0.3158	0.090*
C24	0.4486(3)	0.6961(3)	0.21650(19)	0.0825(7)
H24	0.4748	0.7518	0.2516	0.099*
C25	0.3927(3)	0.7517(2)	0.1270(2)	0.0781(7)
H25	0.3800	0.8454	0.1004	0.094*
N1	0.3563(2)	0.66954(17)	0.07771(12)	0.0611(4)
H1A	0.321(3)	0.707(2)	0.0169(15)	0.073*
O1	0.19842(17)	0.08873(11)	0.03352(8)	0.0512(3)
O2	0.21094(17)	0.30021(11)	0.05712(8)	0.0523(3)
O3	0.09247(15)	0.12874(12)	0.17660(8)	0.0546(3)
O4	0.42123(15)	0.09631(12)	0.15389(8)	0.0537(3)
O5	0.7172(2)	0.23705(15)	0.10376(11)	0.0744(4)
H5A	0.636(2)	0.184(2)	0.1239(14)	0.089*
H5B	0.823(2)	0.192(2)	0.1328(14)	0.089*
B1	0.2307(3)	0.1539(2)	0.10424(14)	0.0491(5)

they are generally readily prepared, are air- and water-stable, and have relatively low toxicities [2]. The discovery of these simple boron compounds become significant owing to their

displaying a wide range of biological properties [3]. The structures of borates are largely complex, and borates possessing novel structures that exhibit great variety potential applications notably in mineralogy and nonlinear optics (NLO) has been well documented [4, 5]. The coordination mode of boron in borate complexes is mostly either a BO<sub>3</sub> triangle or a BO<sub>4</sub> tetrahedron that linked together by the sharing of oxygen atoms. The resulting anionic entities may eventuate in isolated chains, rings, or cages, or may condense further to form polymeric chains, sheets or three-dimensional networks [6, 7]. The non-shared oxygen atoms will either bear a further negative charge (anhydrous borates) or will be protonated (hydrated borates). Hydrated borates are typically further hydrated by water molecules [8]. Most borates synthesized and studied to date have been prepared under the templating effect of cations, such as alkali-metal, alkaline-earth metal, transition metal, main group metal, rare earth metal, and inorganic-organic hybrid borates. Arylspiroboranate esters are a significant class of compounds being of special importance consisting of two catecholato groups linked to central boron atom. These compounds offers a number of advantageous such as being nontoxic, inexpensive and thermally, chemically and electrochemically stable and have found extensive usage in chemistry and industry. To set an example, lithium salts of arylspiroboranate esters are being considered for their potential use as electrolytes in batteries [9]. Other applications of these particular type of compounds involve a use as catalysts, or co-catalysts, for the Diels-Alder reaction [10], methoxycarbonylation reactions [11], and in amide and ester condensation reactions [12]. As part of our ongoing study of the synthesis and structure of organoborate complexes [13–16], we have prepared a new organically templated borate using pyridine as the structure-directing agent.

The asymmetric unit of title compound consists of one [BO<sub>4</sub>(C<sub>10</sub>H<sub>6</sub>)<sub>2</sub>]<sup>-</sup> anion, one [C<sub>5</sub>H<sub>5</sub>NH]<sup>+</sup> cation and one water molecule. The [BO<sub>4</sub>(C<sub>10</sub>H<sub>6</sub>)<sub>2</sub>]<sup>-</sup> anion consists of one set of distorted [BO<sub>4</sub>] tetrahedra and two sets of [C<sub>20</sub>H<sub>12</sub>] planes with oxygen atoms as sharing vertexes. The boron atom is bonded to four oxygen atoms to form a tetrahedral environment (mean O–B–O bond angle of 109.5°). Bond distances and angles are similar to those reported in related arylspiroborate compounds [17–19]. Unsurprisingly, the cyclic ring structure induces a contraction of the O–B–O angles in the five membered rings, with O(1)–B(1)–O(2) 105.45(14)° and O(3)–B(1)–O(4) 103.58(14)°. The exocyclic angles of O(1)–B(1)–O(3) 111.46(14)°, O(2)–B(1)–O(3) 112.09(15)°, O(1)–B(1)–O(4) 112.70(15)°, and O(2)–B(1)–O(4) 111.75(14)° are substantially larger. In the crystal structure [BO<sub>4</sub>(C<sub>10</sub>H<sub>6</sub>)<sub>2</sub>]<sup>-</sup> anion and [C<sub>5</sub>H<sub>5</sub>NH]<sup>+</sup> cation are discrete units and they interact both electrostatically and *via* N–H···O and O–H···O hydrogen bonds with N–O distance is 2.696(2) Å. The water molecule is

also involved in a normal, slightly bent, hydrogen bond with the borate anion at a distance of 2.788(17) Å. The stabilization of the crystal structure arises from electrostatic interactions and is assisted by intermolecular O—H···O and N—H···O hydrogen bonds between the layers.

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