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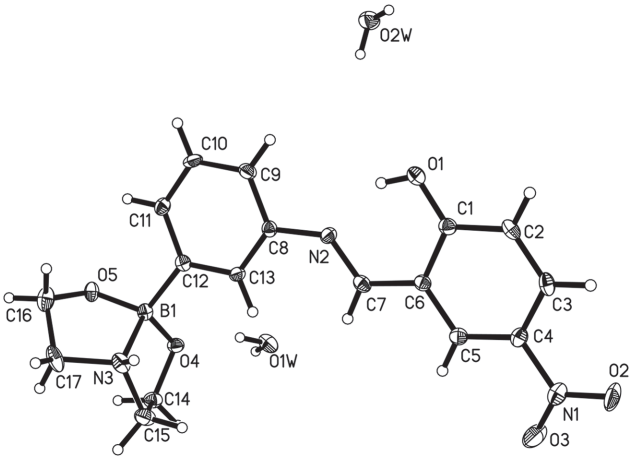
Chunhua Ge, Juanjuan Liu, Zhe Xü, Yang Zhang and Xiangdong Zhang*

Crystal structure of (*E*)-4-nitro-2-(((3-(tetrahydro-8λ^4-[1,3,2]oxazaborolo[2,3-*b*][1,3,2]oxaborol-8-yl)phenyl)imino)methyl)phenol – water (1/2), $C_{17}H_{18}BN_3O_5 \cdot 2H_2O$



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Abstract

The title compound has been synthesized and characterized by IR, ^{1}H NMR, elemental analysis as well as single crystal X-ray diffraction techniques. Crystal structure analysis reveals that the boron atom is tetrahedrally bonding with one carbon atom, one nitrogen atom, and two oxygen atoms. The bond between nitrogen atom and boron atom is a coordination bond.

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Table 1: Data collection and handling.

Crystal:	Yellow, block, size 0.35×0.35×0.41 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	1.10 cm^{-1}
Diffractometer, scan mode:	Bruker SMART CCD area-detector, φ and ω scans
$2\theta_{max}$:	52.12°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	10882, 3487
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2952
$N(param)_{refined}$:	274
Programs:	SHELXS-97 [2]

Table 2: Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	*x*	*y*	*z*	U_{iso}
H(1)	4*a*	0.3206	−0.2802	0.1145	0.048
H(9)	4*a*	0.3225	0.1499	0.2116	0.032
H(7)	4*a*	0.1542	−0.2022	0.093	0.029
H(11)	4*a*	0.1942	0.6409	0.315	0.032
H(14A)	4*a*	−0.0701	0.4991	0.1829	0.036
H(14B)	4*a*	−0.0617	0.6399	0.256	0.036
H(13)	4*a*	0.1203	0.1111	0.1747	0.026
H(3)	4*a*	0.294	−1.0081	−0.0655	0.034
H(2A)	4*a*	0.3674	−0.7896	0.0083	0.032
H(5)	4*a*	0.1374	−0.5414	0.0027	0.03
H(10)	4*a*	0.3035	0.4911	0.2937	0.036
H(17A)	4*a*	0.0115	0.2082	0.4088	0.046
H(17B)	4*a*	−0.0391	0.4291	0.3774	0.046
H(15A)	4*a*	−0.0791	0.1844	0.2842	0.043
H(15B)	4*a*	−0.0312	0.0811	0.2237	0.043
H(16A)	4*a*	0.0434	0.707	0.4214	0.044
H(16B)	4*a*	0.1022	0.4977	0.4022	0.044
H(2WB)	4*a*	0.427(2)	0.753(8)	0.056(2)	0.06(1)
H(2WA)	4*a*	0.490(3)	0.66(1)	0.047(3)	0.08(2)
H(1WB)	4*a*	0.011(2)	0.850(8)	0.065(2)	0.06(1)
H(1WA)	4*a*	0.042(2)	0.671(8)	0.114(2)	0.05(1)
H(1A)	4*a*	0.043(2)	0.083(7)	0.306(2)	0.04(1)

Source of material

All commercially available starting materials were used without additional purification. [3-[(2-Hydroxyl-5-nitrophenyl)-methylene]amino]phenyl boronic acid (Hnapb) was obtained following the general procedure for the synthesis of Schiff bases [1]. 2-Hydroxy-5-nitrobenzaldehyde (10 mmol) and 3-aminophenylboronic acid (10 mmol) were dissolved in methanol (30 ml) and the resulting solution was stirred 12 h

***Corresponding author: Xiangdong Zhang,** College of Chemistry, Liaoning University, Shenyang 110036, China, e-mail: xdzhang@lnu.edu.cn
Chunhua Ge, Juanjuan Liu, Zhe Xü and Yang Zhang: College of Chemistry, Liaoning University, Shenyang 110036, China

Table 3: Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O(2W)	4*a*	0.4688(2)	0.8180(6)	0.0496(1)	0.036(2)	0.043(2)	0.051(2)	−0.008(1)	0.003(1)	−0.002(1)
O(1W)	4*a*	0.0379(1)	0.6918(5)	0.0702(1)	0.030(2)	0.048(2)	0.037(2)	0.005(1)	0.005(1)	0.010(1)
O(4)	4*a*	0.0265(1)	0.5737(4)	0.2081(1)	0.022(1)	0.028(1)	0.026(1)	−0.0021(9)	−0.003(1)	0.0019(9)
N(2)	4*a*	0.2406(1)	−0.1091(5)	0.1364(1)	0.025(2)	0.024(1)	0.022(1)	−0.003(1)	−0.001(1)	−0.002(1)
O(5)	4*a*	0.0672(1)	0.7078(4)	0.3218(1)	0.035(1)	0.021(1)	0.023(1)	0.0077(9)	0.002(1)	−0.0013(9)
O(1)	4*a*	0.3416(1)	−0.3903(5)	0.0904(1)	0.023(1)	0.040(1)	0.034(1)	0.005(1)	0.002(1)	−0.008(1)
C(4)	4*a*	0.2088(2)	−0.7904(6)	−0.0383(2)	0.031(2)	0.022(2)	0.025(2)	0.000(1)	−0.001(2)	−0.002(1)
C(1)	4*a*	0.2998(2)	−0.5173(6)	0.0510(2)	0.022(2)	0.028(2)	0.022(2)	−0.002(1)	0.000(1)	0.003(1)
O(2)	4*a*	0.1850(1)	−1.1257(5)	−0.1192(1)	0.062(2)	0.037(1)	0.043(2)	0.008(1)	−0.003(1)	−0.024(1)
C(9)	4*a*	0.2783(2)	0.2110(6)	0.2208(2)	0.019(2)	0.027(2)	0.033(2)	0.001(1)	0.003(2)	−0.003(1)
C(6)	4*a*	0.2277(2)	−0.4498(6)	0.0493(2)	0.021(2)	0.022(2)	0.022(2)	−0.002(1)	0.002(1)	0.002(1)
N(3)	4*a*	0.0222(1)	0.2509(5)	0.3038(1)	0.031(2)	0.017(1)	0.036(2)	0.008(1)	0.008(1)	0.002(1)
C(7)	4*a*	0.2007(2)	−0.2425(6)	0.0941(2)	0.022(2)	0.028(2)	0.024(2)	0.002(1)	0.003(1)	0.006(1)
N(1)	4*a*	0.1629(2)	−0.9324(5)	−0.0855(1)	0.043(2)	0.027(2)	0.030(2)	0.002(1)	−0.005(1)	−0.003(1)
O(3)	4*a*	0.1038(1)	−0.8491(5)	−0.0907(2)	0.043(2)	0.048(2)	0.071(2)	0.009(1)	−0.021(2)	−0.027(1)
C(11)	4*a*	0.2012(2)	0.5033(6)	0.2822(2)	0.030(2)	0.023(2)	0.026(2)	−0.000(1)	−0.001(1)	−0.006(1)
C(14)	4*a*	−0.0423(2)	0.5058(6)	0.2244(2)	0.024(2)	0.028(2)	0.038(2)	0.001(1)	−0.002(2)	−0.001(1)
C(13)	4*a*	0.1568(2)	0.1885(6)	0.1987(2)	0.021(2)	0.024(2)	0.022(2)	−0.004(1)	−0.002(1)	−0.001(1)
C(3)	4*a*	0.2781(2)	−0.8680(6)	−0.0368(2)	0.036(2)	0.022(2)	0.027(2)	0.008(1)	0.009(2)	−0.001(1)
C(2)	4*a*	0.3218(2)	−0.7355(6)	0.0071(2)	0.023(2)	0.028(2)	0.029(2)	0.008(1)	0.007(2)	0.004(1)
C(12)	4*a*	0.1446(2)	0.3945(5)	0.2477(1)	0.025(2)	0.017(1)	0.021(2)	−0.001(1)	0.002(1)	0.005(1)
C(5)	4*a*	0.1835(2)	−0.5873(6)	0.0041(2)	0.024(2)	0.025(2)	0.026(2)	−0.001(1)	−0.000(1)	0.001(1)
C(10)	4*a*	0.2670(2)	0.4146(6)	0.2696(2)	0.021(2)	0.034(2)	0.035(2)	−0.007(1)	−0.007(2)	−0.008(1)
C(8)	4*a*	0.2229(2)	0.0992(6)	0.1859(1)	0.024(2)	0.020(2)	0.021(2)	−0.001(1)	0.002(1)	0.000(1)
C(17)	4*a*	0.0069(2)	0.3546(6)	0.3749(2)	0.049(2)	0.031(2)	0.036(2)	0.017(2)	0.020(2)	0.006(2)
C(15)	4*a*	−0.0381(2)	0.2247(6)	0.2579(2)	0.027(2)	0.029(2)	0.053(2)	−0.002(1)	0.007(2)	−0.007(2)
B(1)	4*a*	0.0690(2)	0.4988(6)	0.2672(2)	0.027(2)	0.016(2)	0.024(2)	0.001(1)	0.002(2)	0.000(1)
C(16)	4*a*	0.0592(2)	0.5767(7)	0.3868(2)	0.051(2)	0.034(2)	0.026(2)	0.015(2)	−0.003(2)	0.001(1)

under room temperature. The resulting yellow solid was then washed with ethanol to afford product, yield 87.5%, m.p. >300 °C. IR (KBr, cm^{-1}) 3429, 3067, 1626, 1561, 1514, 1478, 1341, 702. ^{1}H NMR (DMSO-d_6): 7.12 (1 H, d, Ar**H**), 7.46–7.57 (2 H, m, Ar**H**), 7.78 (1 H, d, Ar**H**), 7.87 (1 H, s, Ar**H**), 8.23 (2 H, s, BO**H**), 8.25–8.28 (1 H, t, Ar**H**), 8.70 (1 H, d, Ar**H**), 9.21 (1 H, s, C**H**=N), 14.80 (1 H, s, O**H**).

The title compound was prepared from Hnapb and diethanolamine. To CH_3CN (25 mL) containing Hnapb (0.5 mmol), diethanolamine (0.5 mmol) in CH_2Cl_2 (25 mL) were added sequentially. The reaction mixture was stirred under reflux for 12 h, then allowed to cool to r.t.. The resulting yellow amorphous solid was filtered, washed with absolute ethanol and dried. Yield 89.4%, m.p. 222.5–222.7 °C. IR (KBr, cm^{-1}) 3435, 2872, 1617, 1593, 1560, 1409, 1485, 1340, 700. ^{1}H NMR (DMSO-d_6): 2.89–2.90 (2 H, m, C**H**$_2$), 3.12–3.17 (2 H, m, C**H**$_2$), 3.82–3.85 (2 H, m, C**H**$_2$), 3.90–3.93 (2 H, m, C**H**$_2$), 7.02 (1 H, d, Ar**H**), 7.04 (1 H, s, Ar**H**), 7.33–7.37 (1 H, m, Ar**H**), 7.47 (1 H, d, Ar**H**), 7.53 (1 H, s, Ar**H**), 8.22–8.24 (1 H, q, Ar**H**), 8.72 (1 H, d, Ar**H**), 9.26 (1 H, s, C**H**=N), 15.25 (1 H, s, ArO**H**). Anal. Calcd. for $C_{17}H_{22}BN_3O_7$: C, 52.20; H, 5.67; N, 10.74. Found: C, 52.19; H, 5.69; N, 10.74.

Crystals suitable for X-ray analysis were obtained by recrystallization of the product in acetonitrile.

Experimental details

Data were corrected for absorption using the SADABS program [3]. H atoms were treated by a mixture of independent and constrained refinement. All H atoms, except hydrogen atom of water, were positioned geometrically and refined using riding model, with C(sp^2)-H = 0.93 Å, C(sp^3)-H = 0.97 Å, O—H = 0.82 Å and with U_{iso}(H) = 1.2 U_{eq}(C) and 1.5 U_{eq}(O), respectively. All the calculations were performed using the WINGX System, Ver 1.70.01 [4].

Discussion

The significant contemporary interest in boronic acids for covalent organic assembly reflects a desire for exploitation of new materials with a wider range of physical properties. Boronic acids have being utilized as building blocks for the construction of molecular nanostructures and polymeric materials [5]. Condensation reactions of boronic acids can give covalent organic frameworks (COFs), which were linked by boroxine or boronate ester units,

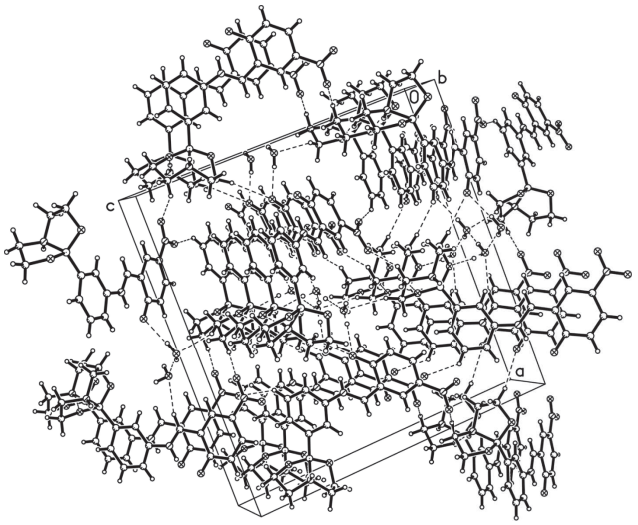

Figure 1: The packing diagram of the title compound, showing supramolecular network.

exhibiting high apparent surface areas and good thermal stabilities [6–8]. Synthetic strategies for the formation of boron-based macrocycles, cages, dendrimers, rotaxanes by multicomponent self-assemblies have also been described [9–11]. For organic boron compounds, the boron center is in a planar sp^2 hybridization with vacant p orbital. It can accept lone pair electrons of a Lewis base such as pyridine or other nitrogen-containing ligands to form Lewis acid-base adducts. Schiff base derivatives of 3-aminophenylboronic acid and substituted salicylaldehyde are used to built polymeric structures through donor- acceptor intermolecular interactions. However, Barba et al. found that electron-withdrawing substituents in 3,5-positions of the salicylaldehyde would reduce the ability of nitrogen and oxygen atoms to coordinate to the boron atom [12]. The reason is suggested that the groups with negative inductive effects would reduce the donor character of the nitrogen and oxygen atoms through the π conjugated system. The molecular structure of the title compound can be divided into two parts. Part one is the [(2-hydroxyl-5-nitrophenyl)methylene]amino]phenyl group and the part two is the diethanolamine adduct of boronic acid. The boron atom is in a tetrahedral environment. B—O bond lengths are 1.459(4) and 1.463(4) Å. The dative B—N bond is 1.668(4) Å indicating its coordinating nature. Part one is nearly planar. The dihedral angle between the two phenyl rings is 5.65°. The intermolecular interaction occurs through π-π stacking of part one. The planes are parallel to each other with a distance of 3.38 Å. The hydroxyl and the methylene amino group form an intramolecular hydrogen bond [O1···N2 = 2.559 Å, O1—H1···N2 = 149°]. Each molecule of title compound contacts to others by an intermolecular hydrogen bond [N3···O5 (symmetry code: x, $-1+y$, z) = 2.2.797 Å, N3—H1A···O5 = 167°]. The above mensioned intermolecular π-π stacking contacts and intermolecular hydrogen bond link molucules to form chains. Water molecules are further linked to these chains to form two dimensional layer [O2W···O1 = 2.798 Å, O2W—H2WB···O1 = 168°; O2W···O1W (symmetry code: $1/2+x$, $1-y$, z) = 2.843 Å, O2W—H2WA···O1W = 164°; O1W···O2W (symmetry code: $-1/2+x$, $2-y$, z) = 2.762 Å, O1W—H1WB···O2W = 173°; O1W···O4 (symmetry code: x, $1-y$, z) = 2.736 Å, O1W—H1WA···O4 = 164°] (Figure 1).

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