

(2-Methoxy-3-pyridyl)boronic acid

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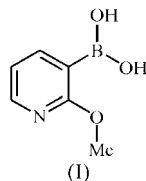
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The structure of the title compound, 2-CH₃O-C₅H₃N-3-B(OH)₂ or C₆H₈BNO₃, comprises two crystallographically independent molecules. The molecules are linked to each other by intermolecular O—H...N and C—H...O bonds to produce an infinite chain, while a two-dimensional structure is formed as a result of π – π interactions of planar molecules.

Comment

Recently, pyridylboronic acids have aroused growing interest because of their important applications (Tyrrell & Brookes, 2004). However, their structures are relatively unexplored when compared with those of the benzene analogues [for crystal structures of related pyridylboronic acids, see Parry *et al.* (2002) and Thompson *et al.* (2005)]. A pyridine N atom bearing a lone electron pair provides an increased potential for extended supramolecular organization *via* hydrogen-bonding interactions. This possibility has prompted us to determine the structure of the title compound, (I). It contains two independent molecules, *A* and *B*, whose geometries differ only marginally (Table 1); the molecular structure of molecule *A* is shown in Fig. 1. Both molecules are essentially planar, the methoxy groups being only slightly twisted. In both molecules, the boronic acid groups have an *exo-endo* conformation. The *endo*-oriented OH groups are engaged in intramolecular O—H...O bonds with methoxy O atoms, thus producing nearly planar six-membered rings. Accordingly, the methoxy group adopts a *syn* conformation with respect to the C—N bond of the pyridine ring.



Unlike most arylboronic acids, (I) does not form centrosymmetric dimers as a result of hydrogen-bonding interactions of the boronic acid groups (Rettig & Trotter, 1977); such interactions are responsible for extended supramolecular

organization in systems based on di- and tetraboronic acids (Fournier *et al.*, 2003; Rodriguez-Cuamatzi *et al.*, 2004), and dimeric units also exist in the crystal structures of isomeric 2-methoxypyridine-5-boronic acid (Thompson *et al.*, 2005) and related 2-chloro- and 2-bromopyridine-5-boronic acids (Parry *et al.*, 2002). In the structure of (I), alternate *A* and *B* molecules are linked in a unique fashion by means of almost linear O—H...N bridges, supported by relatively short C—H...O interactions (Table 2). The boronic acid groups and the N1/C5/H5 units of the pyridine rings act simultaneously as H-atom donors and acceptors, forming approximately planar seven-membered rings. As a result, an infinite zigzag chain is formed (Fig. 2) which can be described as a planar system of fused six- and seven-membered rings. There is only one more example of a simple arylboronic acid, namely 4-formylphenylboronic acid, which does not form centrosymmetric dimers and is assembled primarily in a 'head-to-tail' fashion *via* hydrogen-bonding interactions of boronic acid and formyl groups (Fronczek *et al.*, 2001). A related situation is observed in a few other compounds. In *L*-*p*-boronophenylalanine (Shull *et al.*, 2000), interactions between boronic acid groups and zwitterionic amino acid units are preferred, whereas in the monohydrates of 2-acetylphenylboronic (Ganguly *et al.*, 2003) and 5-pyrimidineboronic acids (Saygili *et al.*, 2004), the presence of water must be taken into account in the interpretation of the crystal packing.

The extended supramolecular assembly consists of the aforementioned hydrogen-bonded chains of molecules, aligned along the crystallographic [102] direction, organized perpendicular to this by π – π interactions between alternate molecules; one of the pair of crystallographically independent molecules in the asymmetric unit is involved in such an interaction, while the other molecule is involved in a C—H... π interaction with its perpendicular partner (Fig. 3). As a result of the π – π interactions, the pyridine rings are stacked in a face-to-face centre-to-edge fashion (Cozzi *et al.*, 2003). Atom N1A is located approximately over the centre of the pyridine

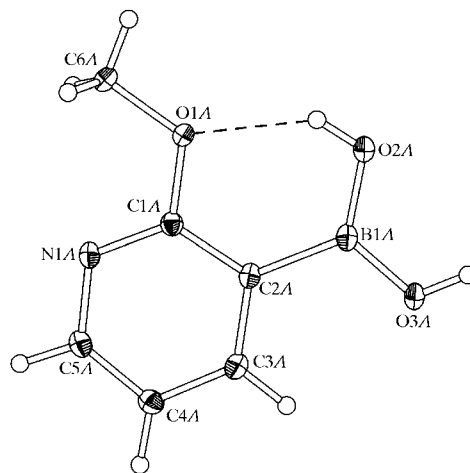
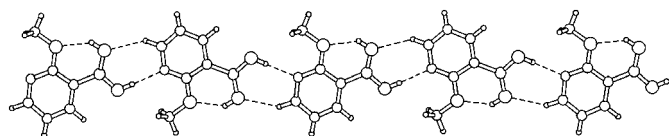
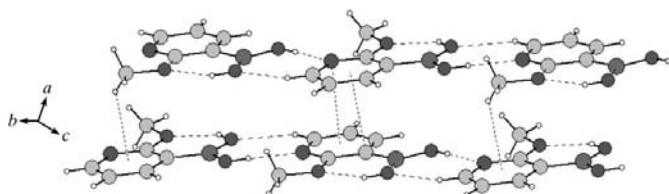


Figure 1

The molecular structure of molecule *A* of (I), showing the atom-labelling scheme. Displacement ellipsoids for all non-H atoms are drawn at the 50% probability level.

**Figure 2**

The hydrogen-bonding pattern for (I). Hydrogen bonds are shown as dashed lines.

**Figure 3**

The crystal packing for (I), showing π - π and C-H... π interactions between hydrogen-bonded chains as dotted lines. Hydrogen bonds are shown as dashed lines.

ring of its partner *B* molecule; the distances to the ring atoms lie in a narrow range between 3.571 (2) [N1A...C1Bⁱⁱⁱ; symmetry code: (iii) $x + 1, y, z + 1$] and 3.622 (2) Å (N1A...C4Bⁱⁱⁱ), whereas the distance to the ring centre at $(-x + 2, -y + 1, -z + 4)$ is 3.327 (1) Å. For atom C2B, the distance to the ring centre of the perpendicular partner *A* at $(-x, -y + 1, -z + 2)$ is 3.375 (1) Å. C-H... π interactions occur between the methoxy group of molecule *B* and the pyridine ring of molecule *A*; the distance of atom H6F from the ring centre at $(-x + 1, -y + 1, -z + 2)$ is 2.767 (14) Å.

In conclusion, the one-dimensional supramolecular organization of (I) achieved *via* intra- and intermolecular hydrogen-bonding interactions is unique among arylboronic acids. In addition, specific π - π interactions form a two-dimensional layer structure.

Experimental

Compound (I) was prepared according to a published procedure (Thompson *et al.*, 2005). Crystals suitable for single-crystal X-ray diffraction analysis were grown by slow evaporation of a saturated solution in ethyl acetate-acetone (1:1) (m.p. 412–413 K).

Crystal data

$\text{C}_6\text{H}_8\text{BNO}_3$	$Z = 8$
$M_r = 152.94$	$D_x = 1.453 \text{ Mg m}^{-3}$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 7.6342$ (3) Å	$\mu = 0.11 \text{ mm}^{-1}$
$b = 25.7404$ (10) Å	$T = 102$ (2) K
$c = 7.2444$ (3) Å	Prism, colourless
$\beta = 100.857$ (3)°	$0.77 \times 0.51 \times 0.31 \text{ mm}$
$V = 1398.10$ (10) Å ³	

Data collection

Oxford Diffraction KM-4-CCD diffractometer	25489 measured reflections
ω scans	3355 independent reflections
Absorption correction: multi-scan (CrysAlis RED; Oxford Diffraction, 2005)	2873 reflections with $I > 2\sigma(I)$
$T_{\min} = 0.94, T_{\max} = 0.97$	$R_{\text{int}} = 0.012$
	$\theta_{\max} = 28.0^\circ$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.055P)^2 + 0.197P]$
$R[F^2 > 2\sigma(F^2)] = 0.030$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.090$	$(\Delta/\sigma)_{\max} = 0.001$
$S = 1.11$	$\Delta\rho_{\max} = 0.38 \text{ e Å}^{-3}$
3355 reflections	$\Delta\rho_{\min} = -0.19 \text{ e Å}^{-3}$
264 parameters	Extinction correction: SHELXL97
All H-atom parameters refined	Extinction coefficient: 0.0061 (12)

Table 1

Selected geometric parameters (Å, °).

O1A—C1A	1.3612 (11)	O1B—C1B	1.3622 (11)
O1A—C6A	1.4408 (11)	O1B—C6B	1.4404 (11)
O2A—B1A	1.3641 (12)	O2B—B1B	1.3663 (12)
O3A—B1A	1.3533 (12)	O3B—B1B	1.3531 (12)
C2A—B1A	1.5763 (13)	C2B—B1B	1.5758 (13)

O1A—C1A—C2A	116.40 (8)	O1B—C1B—C2B	116.44 (8)
C1A—C2A—B1A	124.58 (8)	C1B—C2B—B1B	124.68 (8)
O3A—B1A—O2A	120.40 (8)	O3B—B1B—O2B	120.79 (9)
O3A—B1A—C2A	117.02 (8)	O3B—B1B—C2B	117.04 (8)
O2A—B1A—C2A	122.57 (8)	O2B—B1B—C2B	122.17 (8)

C6A—O1A—C1A—N1A	−3.65 (12)	C6B—O1B—C1B—N1B	3.73 (12)
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Table 2

Hydrogen-bond geometry (Å, °).

$D\cdots H\cdots A$	$D\cdots H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O3B—H3OB...N1A ⁱ	0.866 (17)	1.992 (17)	2.8567 (10)	176.6 (15)
O2B—H2OB...O1B	0.850 (17)	1.999 (17)	2.7272 (9)	143.1 (15)
O3A—H3OA...N1B	0.871 (17)	1.996 (17)	2.8666 (10)	177.3 (15)
O2A—H2OA...O1A	0.840 (16)	2.026 (16)	2.7323 (10)	141.3 (14)
C5A—H5A...O2B ⁱⁱ	0.961 (12)	2.376 (12)	3.245 (1)	150.2 (10)
C5B—H5B...O2A	0.965 (12)	2.390 (12)	3.241 (1)	148.1 (10)

Symmetry codes: (i) $x - 1, y, z - 2$; (ii) $x + 1, y, z + 2$.

All H atoms were located in difference syntheses and refined freely [$C-H = 0.945$ (13)– 0.980 (13) Å].

Data collection: CrysAlis CCD (Oxford Diffraction, 2005); cell refinement: CrysAlis RED (Oxford Diffraction, 2005); data reduction: CrysAlis RED; program(s) used to solve structure: SHELXS97 (Sheldrick, 1990); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: DIAMOND (Brandenburg, 1999); software used to prepare material for publication: SHELXL97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: HJ3025). Services for accessing these data are described at the back of the journal.

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