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# 2-(Methoxycarbonyl)phenylboronic acid

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The structure of the title compound,  $2(CH_3OCO)C_6H_4B-(OH)_2$  or  $C_8H_9BO_4$ , involves two crystallographically independent conformers, *A* and *B*, in a 1:2 ratio; molecules of conformer *A* are located on a crystallographic mirror plane. The most striking difference between the two independent molecules is the opposite orientation of the methoxycarbonyl groups, while the conformations of the boronic acid groups vary more subtly. Molecules of both types are ordered to produce a specific hydrogen-bonding network that can be interpreted in terms of a layer lying parallel to (100). Within the layer, *B* molecules are linked with each other by two different  $O-H\cdots O$  bonds to form an infinite chain where two centrosymmetric dimeric motifs can be distinguished.

#### Comment

The use of arylboronic acids in supramolecular assembly is potentially promising (Fournier *et al.*, 2003; Davis *et al.*, 2001) but still relatively unexplored. Arylboronic acids with carbonyl substituents are interesting as they may be able to support supramolecular organization *via* hydrogen-bonding interactions. For this reason, we have determined the structure of the title compound, (I), for crystal structures of related arylboronic acids (see Fronczek *et al.*, 2001; Ganguly *et al.*, 2003; Scouten *et al.*, 1994; Zarychta *et al.*, 2004).



The structure of (I) is unusual in that it displays conformational isomerism, in contrast to the related compounds cited above. It contains two independent molecules (Fig. 1), one of which (A) lies with all non-H atoms except atom O2Aon a crystallographic mirror plane, while the other (B) occupies a general position. In molecule A, the methoxycarbonyl group is coplanar with the ring by symmetry. The carbonyl group in molecule A is *syn*-directed with respect to the boronic acid group, which resembles the situation in 2-acetylphenylboronic acid monohydrate (Ganguly et al., 2003). In contrast, the carbonyl group in molecule B is anti with respect to the boronic acid group. The methoxycarbonyl group in molecule B is not strictly coplanar with the benzene ring; the C4B-C5B-C10B-O11B torsion angle is 165.22 (10)°, which may reflect steric repulsion between functional groups. Some variation of bond lengths and angles is also observed. The C10-O11 bond in molecule B is longer than the corresponding bond in A (Table 1). Presumably, this effect can be rationalized in terms of hydrogen-bonding interaction between the carbonyl O atom and an OH group from a neighbouring molecule B (Fig. 2), which slightly decreases the C10B-O11B bond order. The C4-C5-C10 bond angles are 117.65 (12) and 121.05 (9) $^{\circ}$ , whereas the C6-C5-C10 bond angles are 120.73 (12) and 117.27 (9)° for molecules A and B, respectively. The situation in molecule A is similar to that observed in 2-acetylphenylboronic acid (Ganguly et al., 2003). It is plausible that a weak boron-oxygen interaction  $[B1A \cdots O11A = 2.628 (6) Å]$ , resulting from a partial overlap of an empty 2p orbital of the B atom with the lone pair of the carbonyl O atom, decreases the C4-C5-C10 angle. In molecule B, such an interaction is not possible, and



#### Figure 1

The molecular structures of conformers A (left) and B (right), showing the atom-labelling scheme. Displacement ellipsoids for all non-H atoms are drawn at the 50% probability level.



#### Figure 2

The crystal packing and hydrogen-bonding pattern for (I), with the assigned graph-set motifs (see *Comment*). Hydrogen bonds are shown as dashed lines.

the C4-C5-C10 angle is larger. The conformational isomerism is also reflected in the behaviour of the boronic acid groups. In molecule A, the boronic acid group is rotated more with respect to the ring, as seen from the O2A - B1A - C4A - C4AC5A torsion angle [94.82  $(12)^{\circ}$ ]; in B, the boronic acid group displays a corresponding O2B-B1B-C4B-C9B torsion angle of -71.88 (13)°. Such flexible behaviour of a boronic acid group was found in other ortho-substituted arylboronic acids (Gainsford et al., 1995; Ganguly et al., 2003) but not for the closely related 2-formylphenylboronic acid (Scouten et al., 1994), where the planar conformation is stabilized by an intramolecular hydrogen bond. Another difference is the conformation within B(OH)<sub>2</sub> groups, reflecting a specific crystal packing imposed by intermolecular hydrogen bonding. In molecule A, both OH bonds are syn-directed with respect to the ring, whereas in B they exhibit a syn-anti orientation.

The crystal packing diagram for (I), showing the effect of mirror symmetry, is depicted in Fig. 2. There are three classical  $O-H \cdots O$  hydrogen bonds (the geometry and symmetry codes are given Table 2); the strongest hydrogen bonds,  $O3B-H3B\cdots O11B^{iii}$ , are formed between molecules B (motif a in Fig. 2) (Etter, 1990; Bernstein et al., 1995), producing a centrosymmetric dimer  $[R_2^2(14)]$  graph-set descriptor]. Furthermore, molecules B are linked with one another by  $O2B - H2B \cdots O3B^{ii}$  hydrogen bonds between  $B(OH)_2$  groups (motif b), forming centrosymmetric dimers  $[R_2^2(8) \text{ rings}]$  typical of arylboronic acids (Rettig & Trotter, 1977). Molecules A are linked to boronic acid O atoms of two adjacent molecules B by an  $O2A - H2A \cdots O2B$  bridge [motif c,  $D_2^2(7)$  graph-set descriptor]. The second-level motif  $N_2(ab) =$  $C_2^2(9)[R_4^4(20)]$  depicts a characteristic infinite chain of alternating fused rings. Other chains are represented by binary motifs  $N_2(ac) = C_3^3(15)$  and  $N_2(bc) = C_3^3(10)$ . The hydrogenbond network produces an infinite two-dimensional structure, where a larger ring depicted by the third-level graph-set descriptor  $N_3(abc) = C_4^4(15)[R_8^8(30)]$  can be distinguished.

# **Experimental**

Compound (I) was obtained from Aldrich. Crystals of (I) suitable for single-crystal X-ray diffraction analysis were grown by slow evaporation of a saturated solution in ethyl acetate/toluene (1:1) (m.p. 375–377 K).

Crystal data

$C_8H_9BO_4$ $M_r = 179.96$ Monoclinic P2 (m	Z = 6 $D_x = 1.389 \text{ Mg m}^{-3}$ Mo K a radiation
a = 8.2764 (2) Å	$\mu = 0.11 \text{ mm}^{-1}$
b = 19.7124 (6) Å	T = 100 (2)  K
c = 8.7321 (3) Å	Prism, colourless
$\beta = 115.007 (3)^{\circ}$	$0.46 \times 0.32 \times 0.21 \text{ mm}$
V = 1291.07 (7) Å <sup>3</sup>	
Data collection	
Oxford Diffraction KM-4 CCD	23407 measured reflections
diffractometer	3268 independent reflections
$\omega$ scans	2797 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan	$R_{\rm int} = 0.012$
(CrysAlis RED; Oxford	$\theta_{\rm max} = 28.6^{\circ}$
Diffraction, 2005)	

## Refinement

Refinement on $F^2$	$w = 1/[\sigma^2(F^2) + (0.0537P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.033$	+ 0.2342P]
$vR(F^2) = 0.094$	where $P = (F_0^2 + 2F_c^2)/3$
S = 1.12	$(\Delta/\sigma)_{\rm max} = 0.001$
3268 reflections	$\Delta \rho_{\rm max} = 0.53 \ {\rm e} \ {\rm \AA}^{-3}$
252 parameters	$\Delta \rho_{\rm min} = -0.26 \text{ e } \text{\AA}^{-3}$
All H-atom parameters refined	

## Table 1

Selected geometric parameters (Å, °).

$B1A - O2A^{i}$	1.3616 (11)	B1 <i>B</i> -O3 <i>B</i>	1.3677 (14)
B1A - C4A	1.592 (2)	B1B-C4B	1.5823 (15)
C5A-C10A	1.502 (2)	C5B-C10B	1.4825 (14)
C10A-O11A	1.1951 (17)	C10B-O11B	1.2204 (12)
C10A-O12A	1.3344 (17)	C10B-O12B	1.3280 (12)
B1B-O2B	1.3610 (13)		
024 <sup>i</sup> B14 024	116 24 (12)	$O_{1}P$ $P_{1}P$ $O_{2}P$	119 62 (0)
$O_2A = D_1A = O_2A$	110.54(12)	O2B = B1B = O3B	118.05 (9)
$O_{2A} - B_{1A} - C_{4A}$	121.50 (6)	$O_{2B} = B_{1B} = C_{4B}$	118.41 (9)
C9A - C4A - B1A	119.48 (12)	$O_{3B}$ -BIB-C4B	122.67 (9)
CSA - C4A - BIA	125.59 (12)	C3B = C4B = B1B	122.76 (9)
C6A - C5A - C10A	120.73(12)	$C_{0B} = C_{5B} = C_{10B}$	117.27 (9)
C4A - C5A - C10A	117.65 (12)	C4B = C5B = C10B	121.05 (9)
OIIA - CI0A - OI2A	124.97 (14)	O11B-C10B-O12B	122.72 (9)
O11A - C10A - C5A	123.66 (13)	O11B - C10B - C5B	124.87 (9)
O12A - C10A - C5A	111.37 (12)	O12B - C10B - C5B	112.42 (8)
02	A - B1A - C4A - C	C9A 85.18 (12)	
02	$A^{i}-B1A-C4A-0$	C5A 94.82 (12)	
B1	B-C4B-C5B-C	10B - 1.63 (15)	
Cé	B - C5B - C10B - 0	O11 $B$ -17.14 (15)	
C4	B - C5B - C10B - 0	O11B 165.22 (10)	
Cé	B-C5B-C10B-0	O12B 163.00 (9)	
01	1B - C10B - O12B	-C13B $-3.24$ (14)	

Symmetry code: (i)  $x, -y + \frac{1}{2}, z$ .

Table 2

Tyurogen-bond geometry (A, )	gen-bond geometry (A, ).	Aydrogen-bond	geometry	(A, `	).
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$D - H \cdots A$	D-H	$H \cdot \cdot \cdot A$	$D \cdots A$	$D - \mathbf{H} \cdots A$
$O2A - H2A \cdots O2B$ $O2B - H2B \cdots O3B^{ii}$ $O3B - H3B \cdots O11B^{iii}$	0.883 (17)	1.901 (17)	2.7835 (11)	177.8 (16)
	0.880 (19)	1.870 (19)	2.7451 (11)	172.8 (16)
	0.858 (19)	1.87 (2)	2.7187 (11)	172.6 (18)

Symmetry codes: (ii) -x + 1, -y, -z; (iii) -x + 1, -y, -z + 1.

All H atoms were located in difference syntheses and refined freely [C-H = 0.931 (19)-0.996 (14) 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: *SHELXTL97*.

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 $T_{\rm min} = 0.96, \ T_{\rm max} = 0.98$ 

Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ3006). Services for accessing these data are described at the back of the journal.

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