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(4-Carbamoylphenyl)boronic acid

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 Key indicators: single-crystal X-ray study; $T = 290$ K; mean $\sigma(I) = 0.000$ Å; disorder in main residue; R factor = 0.053; wR factor = 0.148; data-to-parameter ratio = 14.4.

In the title compound, $C_7H_8BNO_3$, the molecule lies on an inversion center leading to a statistical disorder of the $B(OH)_2$ and $CONH_2$ groups. In the crystal structure, molecules are linked by $N-H \cdots O$ and $O-H \cdots O$ hydrogen bonds, forming sheets parallel to the bc plane. The $B(OH)_2$ and $CONH_2$ groups are twisted out of the mean plane of the benzene ring by 23.9 (5) and 24.6 (6)°, respectively.

Related literature

For general background to the use of boronic acids in organic synthesis, as pharmaceutical agents and in crystal engineering see: Miyaura & Suzuki (1995); Suzuki (1999); Adams & Kauffman (2004); Barth *et al.* (2005); Minkkilä *et al.* (2008); Maly *et al.* (2006); Desiraju (1995); James *et al.* (2006).. For related structures, see: Cobbleddick & Small (1972); Rodríguez-Cuamatzi *et al.* (2004). For hydrogen-bond motifs, see: Bernstein *et al.* (1995).



Experimental

Crystal data

$C_7H_8BNO_3$	$\gamma = 93.136$ (14)°
$M_r = 164.95$	$V = 186.36$ (11) Å ³
Triclinic, $P\bar{1}$	$Z = 1$
$a = 4.997$ (2) Å	Mo $K\alpha$ radiation
$b = 5.351$ (2) Å	$\mu = 0.11$ mm ⁻¹
$c = 7.2967$ (16) Å	$T = 290$ K
$\alpha = 103.912$ (13)°	$0.27 \times 0.25 \times 0.25$ mm
$\beta = 98.69$ (2)°	

Data collection

Enraf–Nonius CAD-4 diffractometer	755 reflections with $I > 2\sigma(I)$
2155 measured reflections	$R_{int} = 0.054$
1078 independent reflections	3 standard reflections every 120 min intensity decay: 2%

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.053$	88 restraints
$wR(F^2) = 0.148$	H-atom parameters constrained
$S = 1.03$	$\Delta\rho_{max} = 0.28$ e Å ⁻³
1078 reflections	$\Delta\rho_{min} = -0.23$ e Å ⁻³
75 parameters	

Table 1

Hydrogen-bond geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$O1-H1 \cdots O2^i$	0.82	1.96	2.77 (2)	167
$O2-H2A \cdots O1^{ii}$	0.82	2.05	2.79 (2)	149
$O2-H2A \cdots O3^{iii}$	0.82	2.00	2.73 (2)	149
$N1-H1A \cdots O3^{iv}$	0.86	2.14	2.97 (3)	160.7
$N1-H1B \cdots O1^v$	0.86	2.30	2.97 (2)	135.7
$N1-H1B \cdots O3^{vi}$	0.86	2.18	2.90 (2)	140.8

Symmetry codes: (i) $-x, -y - 1, -z + 1$; (ii) $x + 1, y, z$; (iii) $-x + 1, -y, -z$; (iv) $-x, -y + 1, -z - 1$; (v) $-x - 1, -y, -z$; (vi) $x - 1, y, z$.

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *Mercury* (Bruno *et al.*, 2002); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: LH2998).

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(4-Carbamoylphenyl)boronic acid

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S1. Comment

The title compound possesses two distinct functional groups: boronic acid and amide. Compounds containing the boronic acid moiety are important as precursors for organic transformations (Miyaura & Suzuki, 1995; Suzuki, 1999;) and recently attention has been focused on these types of compounds as potential pharmaceutical agents (Adams & Kauffman, 2004; Barth *et al.*, 2005; Minkkilä *et al.*, 2008). Amides are versatile precursors to many other functional groups and undergo many chemical reactions, usually through an attack on the carbonyl group. The title compound is a commercial product and we solved its crystal structure to verify the repeatability of the weak interactions already observed in the structures of terephthalamide and phenylboronic acid Cobbleddick & Small, 1972; Rodríguez-Cuamatzi, P. *et al.*, 2004. Self assembling based on hydrogen-bonding motifs is of general interest for crystal engineering, structural chemistry and biology (Maly *et al.*, 2006; Desiraju, 1995).

The crystal structure of the studied compound contains molecules linked together by hydrogen bonds in sheets similar to those of terephthalamide (Cobbleddick & Small, 1972) and 1,4-phenilboronic acid (Rodríguez-Cuamatzi *et al.*, 2004) (Fig. 1). More over all three compounds have similar triclinic lattice parameters and crystallize in the centrosymmetric P-1 space group. In the title compound, the location of the molecule on a center of symmetry leads to a statistical disorder of the B(OH)₂ and CONH₂ groups (Fig. 1). The B(OH)₂ and CONH₂ groups are out of the mean plane of the benzene ring by 23.9 (5)° and 24.6 (6)° respectively. Similar angle is reported for the amide group in terephthalamide (23°) while the one for 1,4 phenilboronic acid is greater (~35°). It should be noted that C—C (phenyl-amide) and C—B distances of 1.505 (6) Å and 1.546 (6) Å are restrained to match those in the terephthalamide molecule C—C (phenyl-amide) distance of 1.489 (5) Å and that of the 1,4-phenilboronic acid molecule with C—B of 1.564 (3) Å.

Both amide and boronic acid groups are involved in hydrogen bonds to form ring motifs marked by I and II (Fig. 2). Type I, R₂²(8) (Bernstein *et al.* 1995) connects opposite sides of molecules to chains. Type II links the chains to form sheets parallel to *bc*. However, two type of motifs linking the chains can be proposed: R₄⁴(8) (Fig. 2a) and R₃³(8) (Fig. 2b). Indeed, hydrogen bonding pattern can vary depending on the position of the hydrogen atoms attached to the B(OH)₂ moiety (Fig. 3). The current position of H atoms for the B(OH)₂ group (*syn*, *anti*) results from a SHELX AFIX 147 instruction. As a result the bonding interaction between the B(OH)₂ and amide groups is forbidden, due to the short contact between hydrogen atoms linked to O1 and N1 (H1...H1A 1.272 Å). Thus the hydrogen bonding interactions in the chains are limited to "boronic-boronic" and "amid-amide". An alternative (*anti*, *syn*) positioning for H attached to O will permit hydrogen bonding between B(OH)₂ and amid groups but an F_o map (Fig. 4) does not suggest an (*anti*, *syn*) conformation for the H atoms.

S2. Experimental

The studied compound is a commercial product (Frontier Scientific). Colorless crystals of C₇H₈NBO₃, were obtained after several days staying from 50% water:ethanol solution at 277K.

S3. Refinement

All H atoms were placed in idealized positions ($C-H = 0.93 \text{ \AA}$, $O-H = 0.82 \text{ \AA}$ and $N-H = 0.86 \text{ \AA}$) and were constrained to ride on their parent atoms, with $U_{iso}(H) = 1.2U_{eq}(C, O \text{ or } N)$. Disorder refinement required the introduction of appropriate series of restraints on bond lengths and planarity.

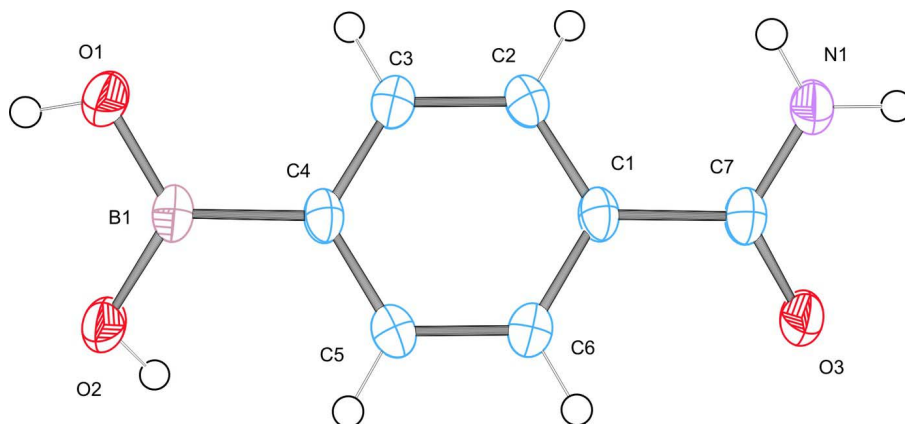


Figure 1

The molecule of title compound with the atom numbering scheme showing 50% probability displacement ellipsoids. H atoms are shown as small spheres of arbitrary radii.

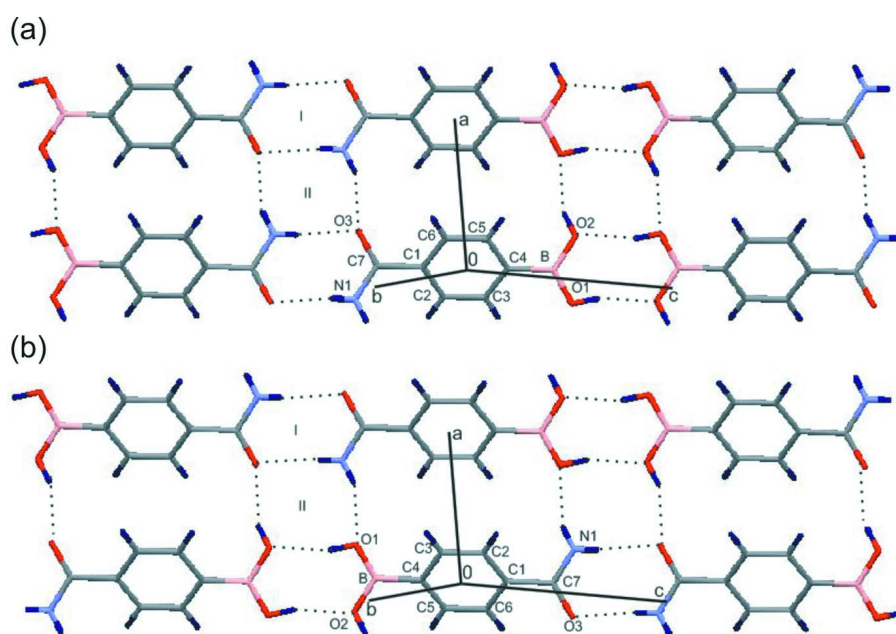


Figure 2

Two possible ways of molecular arrangement in the unit cell, showing the hydrogen-bonding interactions as dashed lines: type I connects opposite sides of molecules to chains and II links the chains together.

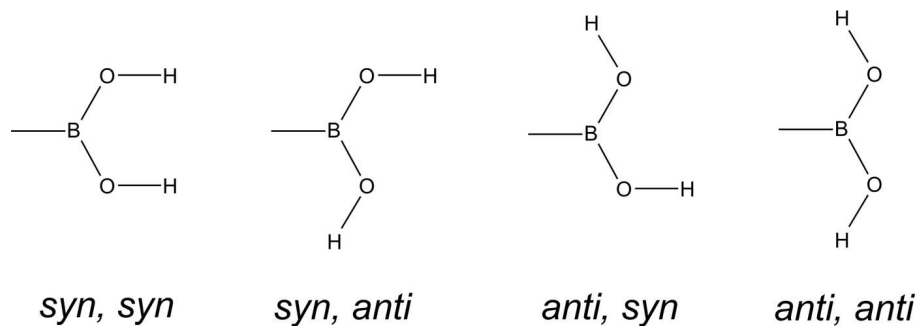


Figure 3
Possible conformations of the B(OH)₂ functional group.

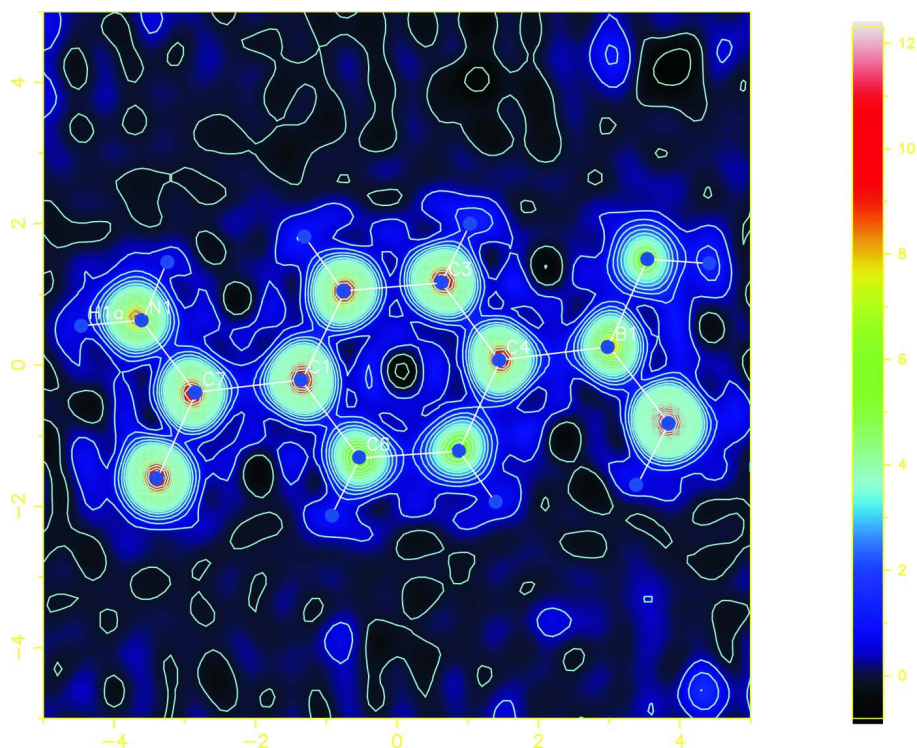


Figure 4
 F_o electron density viewed perpendicular to the mean plane of the molecule.

(4-carbamoylphenyl)boronic acid

Crystal data

$C_7H_8BNO_3$
 $M_r = 164.95$
 Triclinic, $P\bar{1}$
 Hall symbol: -P 1
 $a = 4.997(2) \text{ \AA}$
 $b = 5.351(2) \text{ \AA}$
 $c = 7.2967(16) \text{ \AA}$
 $\alpha = 103.912(13)^\circ$
 $\beta = 98.69(2)^\circ$
 $\gamma = 93.136(14)^\circ$
 $V = 186.36(11) \text{ \AA}^3$

$Z = 1$
 $F(000) = 86$
 $D_x = 1.470 \text{ Mg m}^{-3}$
 Melting point: not measured K
 Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$
 Cell parameters from 22 reflections
 $\theta = 18.0\text{--}19.8^\circ$
 $\mu = 0.11 \text{ mm}^{-1}$
 $T = 290 \text{ K}$
 Prismatic, colorless
 $0.27 \times 0.25 \times 0.25 \text{ mm}$

Data collection

Enraf–Nonius CAD-4 diffractometer	$R_{\text{int}} = 0.054$
Radiation source: fine-focus sealed tube	$\theta_{\text{max}} = 30.0^\circ$, $\theta_{\text{min}} = 2.9^\circ$
Graphite monochromator	$h = -7 \rightarrow 7$
Non-profiled $\omega/2\theta$ scans	$k = -7 \rightarrow 7$
2155 measured reflections	$l = -10 \rightarrow 10$
1078 independent reflections	3 standard reflections every 120 min
755 reflections with $I > 2\sigma(I)$	intensity decay: 2%

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.053$	H-atom parameters constrained
$wR(F^2) = 0.148$	$w = 1/[\sigma^2(F_o^2) + (0.0786P)^2 + 0.0033P]$
$S = 1.03$	where $P = (F_o^2 + 2F_c^2)/3$
1078 reflections	$(\Delta/\sigma)_{\text{max}} = 0.001$
75 parameters	$\Delta\rho_{\text{max}} = 0.28 \text{ e } \text{\AA}^{-3}$
88 restraints	$\Delta\rho_{\text{min}} = -0.23 \text{ e } \text{\AA}^{-3}$
Primary atom site location: structure-invariant direct methods	

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) etc. and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
B1	-0.001 (3)	-0.298 (2)	0.2892 (18)	0.0268 (10)	0.50
O1	-0.243 (3)	-0.393 (3)	0.318 (3)	0.0399 (19)	0.50
H1	-0.2184	-0.4584	0.4092	0.060*	0.50
O2	0.236 (2)	-0.334 (2)	0.404 (2)	0.0351 (15)	0.50
H2A	0.3669	-0.3158	0.3510	0.053*	0.50
C1	0.0096 (17)	0.113 (2)	-0.1593 (16)	0.0246 (10)	0.50
C2	-0.2061 (18)	-0.068 (2)	-0.1647 (17)	0.0314 (10)	0.50
H2	-0.3512	-0.1021	-0.2661	0.038*	0.50
C3	-0.207 (2)	-0.197 (2)	-0.0217 (17)	0.0314 (10)	0.50
H3	-0.3529	-0.3166	-0.0282	0.038*	0.50
C4	0.0069 (18)	-0.150 (2)	0.1318 (16)	0.0246 (10)	0.50
C5	0.2219 (19)	0.029 (2)	0.1375 (17)	0.0314 (10)	0.50
H5	0.3670	0.0634	0.2389	0.038*	0.50
C6	0.223 (2)	0.158 (2)	-0.0057 (17)	0.0314 (10)	0.50
H6	0.3685	0.2776	0.0010	0.038*	0.50
C7	0.016 (2)	0.256 (2)	-0.3128 (15)	0.0268 (10)	0.50

O3	0.237 (3)	0.341 (3)	-0.344 (3)	0.0399 (19)	0.50
N1	-0.212 (3)	0.283 (3)	-0.415 (3)	0.0351 (15)	0.50
H1A	-0.2112	0.3606	-0.5051	0.042*	0.50
H1B	-0.3631	0.2237	-0.3916	0.042*	0.50

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
B1	0.0340 (13)	0.027 (3)	0.024 (2)	0.0062 (15)	0.0098 (12)	0.011 (2)
O1	0.0295 (7)	0.054 (5)	0.048 (4)	0.002 (2)	0.0081 (18)	0.035 (4)
O2	0.0282 (18)	0.046 (4)	0.0412 (16)	0.006 (2)	0.0081 (15)	0.029 (3)
C1	0.0301 (11)	0.028 (3)	0.020 (3)	0.0076 (11)	0.0089 (11)	0.0097 (19)
C2	0.0331 (11)	0.038 (3)	0.024 (3)	-0.0005 (12)	-0.0004 (12)	0.0137 (19)
C3	0.0329 (11)	0.034 (3)	0.030 (3)	-0.0018 (12)	0.0048 (12)	0.015 (2)
C4	0.0301 (11)	0.028 (3)	0.020 (3)	0.0076 (11)	0.0089 (11)	0.0097 (19)
C5	0.0331 (11)	0.038 (3)	0.024 (3)	-0.0005 (12)	-0.0004 (12)	0.0137 (19)
C6	0.0329 (11)	0.034 (3)	0.030 (3)	-0.0018 (12)	0.0048 (12)	0.015 (2)
C7	0.0340 (13)	0.027 (3)	0.024 (2)	0.0062 (15)	0.0098 (12)	0.011 (2)
O3	0.0295 (7)	0.054 (5)	0.048 (4)	0.002 (2)	0.0081 (18)	0.035 (4)
N1	0.0282 (18)	0.046 (4)	0.0412 (16)	0.006 (2)	0.0081 (15)	0.029 (3)

Geometric parameters (Å, °)

B1—O1	1.351 (8)	C3—C4	1.391 (8)
B1—O2	1.393 (8)	C3—H3	0.9300
B1—C4	1.546 (6)	C4—C5	1.391 (8)
O1—H1	0.8200	C5—C6	1.384 (8)
O2—H2A	0.8200	C5—H5	0.9300
C1—C6	1.388 (8)	C6—H6	0.9300
C1—C2	1.397 (8)	C7—O3	1.246 (7)
C1—C7	1.505 (6)	C7—N1	1.298 (7)
C2—C3	1.384 (8)	N1—H1A	0.8600
C2—H2	0.9300	N1—H1B	0.8600
O1—B1—O2	118.9 (15)	C5—C4—B1	122.2 (8)
O1—B1—C4	119.4 (13)	C6—C5—C4	120.8 (5)
O2—B1—C4	121.6 (12)	C6—C5—H5	119.6
C6—C1—C2	117.8 (5)	C4—C5—H5	119.6
C6—C1—C7	120.0 (7)	C5—C6—C1	121.2 (6)
C2—C1—C7	122.2 (7)	C5—C6—H6	119.4
C3—C2—C1	121.1 (5)	C1—C6—H6	119.4
C3—C2—H2	119.5	O3—C7—N1	120.8 (16)
C1—C2—H2	119.5	O3—C7—C1	120.4 (13)
C2—C3—C4	120.8 (5)	N1—C7—C1	118.8 (13)
C2—C3—H3	119.6	C7—N1—H1A	120.0
C4—C3—H3	119.6	C7—N1—H1B	120.0
C3—C4—C5	118.2 (5)	H1A—N1—H1B	120.0
C3—C4—B1	119.5 (8)		

Hydrogen-bond geometry (Å, °)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
O1—H1 \cdots O2 ⁱ	0.82	1.96	2.77 (2)	167
O2—H2A \cdots O1 ⁱⁱ	0.82	2.05	2.79 (2)	149
O2—H2A \cdots O3 ⁱⁱⁱ	0.82	2.00	2.73 (2)	149
N1—H1A \cdots O3 ^{iv}	0.86	2.14	2.97 (3)	160.7
N1—H1B \cdots O1 ^v	0.86	2.30	2.97 (2)	135.7
N1—H1B \cdots O3 ^{vi}	0.86	2.18	2.90 (2)	140.8

Symmetry codes: (i) $-x, -y-1, -z+1$; (ii) $x+1, y, z$; (iii) $-x+1, -y, -z$; (iv) $-x, -y+1, -z-1$; (v) $-x-1, -y, -z$; (vi) $x-1, y, z$.