Acta Cryst E STRUCTURE REPORTS

OPEN ACCESS

ISSN 1600-5368

Crystal structure of (2-benzyloxypyrimidin-5-yl)boronic acid

Krzysztof Durka,* Tomasz Kliś and Janusz Serwatowski

Physical Chemistry Department, Faculty of Chemistry, Warsaw University of Technology, Noakowskiego 3, 00-664 Warsaw, Poland. *Correspondence e-mail: kdurka@ch.pw.edu.pl

Received 24 October 2014; accepted 7 November 2014

Edited by M. Zeller, Youngstown State University, USA

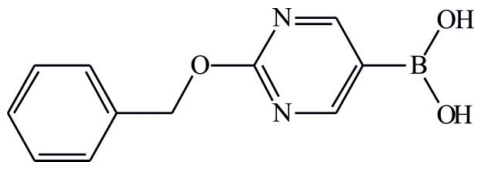
The boronic acid group in the title compound, $C_{11}H_{11}BN_2O_3$, adopts a *syn–anti* conformation and is almost coplanar with the aromatic rings , making a dihedralangle of 3.8 (2)°. In the crystal, adjacent molecules are linked *via* pairs of O—H···O interactions, forming centrosymmetric dimers with an $R_2^2(8)$ motif, which have recently been shown to be energetically very favorable (Durka *et al.*, 2012, 2014). The hydroxy groups in an *anti* conformation are engaged in lateral hydrogen-bonding interactions with N atoms from neighbouring molecules, leading to the formation of chains along [001]. O···B [3.136 (2) Å] and C(π)···B [3.393 (2) Å] stacking interactions in turn link parallel chains of centrosymmetric dimers into layers parallel to (010).

Keywords: crystal structure; arylboronic acid; hydrogen-bonding interactions.

CCDC reference: 937427

1. Related literature

For general background to the structures of boronic acids, see, for example: Hall (2011); Luliński *et al.* (2007); Maly *et al.* (2006); Shimpi *et al.* (2007). For the characterization of related pyrymidylboronic acids, see: Clapham *et al.* (2007); Liao *et al.* (1964); Peters *et al.* (1990); Saygili *et al.* (2004).



2. Experimental

2.1. Crystal data

$C_{11}H_{11}BN_2O_3$
M_r = 230.03
Monoclinic, $P2_1/n$
a = 5.498 (1) Å
b = 30.4320 (17) Å
c = 6.7086 (19) Å
β = 113.54 (4)°
V = 1029.0 (4) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.11 mm^{-1}
T = 100 K
0.20 × 0.15 × 0.15 mm

2.2. Data collection

Kuma KM-4 CCD diffractometer
Absorption correction: multi-scan (*CrysAlis PRO*; Agilent, 2013)
T_{min} = 0.993, T_{max} = 1.000
18472 measured reflections
4167 independent reflections
2975 reflections with $I > 2\sigma(I)$
R_{int} = 0.044

2.3. Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.053
$wR(F^2)$ = 0.135
S = 1.03
4167 reflections
160 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.57 e Å^{-3}
$\Delta\rho_{min}$ = −0.30 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C2—H2···O2^{i}	0.95	2.60	3.5104 (15)	161
O2—H2A···O1^{ii}	0.852 (19)	1.915 (19)	2.7615 (16)	172.7 (17)
O1—H1A···N1^{iii}	0.849 (18)	2.067 (18)	2.8188 (15)	147.2 (16)

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

Data collection: *CrysAlis PRO* (Agilent, 2013); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis PRO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2013* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 2005); software used to prepare material for publication: *publCIF* (Westrip, 2010).

Acknowledgements

The X-ray measurements were undertaken in the Crystallographic Unit of the Physical Chemistry Laboratory at the Chemistry Department of the University of Warsaw. This work was supported by the Aldrich Chemical Co. through donation of chemicals and equipment, and by the Warsaw University of Technology.

Supporting information for this paper is available from the IUCr electronic archives (Reference: ZL2604).

References

Agilent (2013). *CrysAlis PRO*. Agilent Technologies, Santa Clara, USA.
Brandenburg, K. (2005). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.
Clapham, K. M., Smith, A. E., Batsanov, A. S., McIntyre, L., Pountney, A., Bryce, M. R. & Tarbit, B. (2007). *Eur. J. Org. Chem.* pp. 5712–5716.
Durka, K., Jarzembska, K. N., Kamiński, R., Luliński, S., Serwatowski, J. & Woźniak, K. (2012). *Cryst. Growth Des.* **12**, 3720–3734.

Durka, K., Luliński, S., Jarzembska, K. N., Smętek, J., Serwatowski, J. & Woźniak, K. (2014). *Acta Cryst.* B**70**, 157–171.
Hall, D. G. (2011). *Boronic Acids*, pp. 3–8. Weinheim: Wiley-VCH.
Liao, T. K., Podrebarac, E. G. & Cheng, C. C. (1964). *J. Am. Chem. Soc.* **86**, 1869–1870.
Luliński, S., Madura, I., Serwatowski, J., Szatyłowicz, H. & Zachara, J. (2007). *New J. Chem.* **31**, 144–15.
Maly, K. E., Maris, T. & Wuest, J. D. (2006). *CrystEngComm*, **8**, 33–35.
Peters, D., Hörnfeldt, A. B. & Gronowitz, S. (1990). *J. Heterocycl. Chem.* **27**, 2165–2173.
Saygili, N., Batsanov, A. S. & Bryce, M. R. (2004). *Org. Biomol. Chem.* **2**, 852–857.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Shimpi, M. R., SeethaLekshmi, N. & Pedireddi, V. R. (2007). *Cryst. Growth Des.* **7**, 1958–1963.
Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.

supporting information

Acta Cryst. (2014). E**70**, o1259–o1260 [doi:10.1107/S1600536814024519]

Crystal structure of (2-benzyloxypyrimidin-5-yl)boronic acid

Krzysztof Durka, Tomasz Kliś and Janusz Serwatowski

S1. Comment

Heterocyclic boronic acids have been intensively studied in the recent years. They have found numerous application as Suzuki-Miyaura cross-coupling partners. However, pyrimidylboronic acids have been largely neglected, although some derivatives were synthesized (Clapham *et al.*, 2007; Liao *et al.*, 1964; Peters *et al.*, 1990; Saygili *et al.*, 2004). In this manuscript we focus our attention on a pyrimidine boronic acid derivative containing a benzyloxy group at the 2nd position.

The molecular structure of **1** shows that the $B(OH)_2$ group adopts the usual *syn-anti* conformation. The entire molecule including both aromatic rings and boronic group remains essentially planar (Figure 1). On the first level of material organization, centrosymmetric O—H···O hydrogen-bonded dimers are formed. They are linked *via* lateral hydrogen-bonding interactions with nitrogen atoms from neighbouring molecules. It results in the formation of molecular chains propagated along the [001] direction (Figure 2). Molecules from adjacent chains interact by weak O···B and C(π)···B stacking interactions, which link parallel oriented chains into 2D layers. These contacts are additionally supported by weak C—H···N interactions between the methylene group and one of the N atoms of the pyrimidyl ring, and also by C—H···O interactions formed between the C(pyrimidyl)—H group and an oxygen atom from the $B(OH)_2$ group. The supramolecular architecture extends further due to weak C—H···C(π) contacts leading to a three-dimensional network.

S2. Crystallization

The title compound was received from Aldrich. Crystals suitable for single-crystal X-ray diffraction analysis were grown by cooling a solution of the boronic acid (0.2 g) in acetone (4 ml).

S3. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. All CH (methylene, phenyl) hydrogen atoms were placed in calculated positions with C—H distances of 0.95Å (phenyl) and 0.99Å (methylene). They were included in the refinement in riding-motion approximation with U_{iso}(phenyl H)=1.2U_{eq}(C), and U_{iso}(methyl H) = 1.5U_{eq}(C). The positions of OH hydrogen atoms were refined with U_{iso}(hydroxy H) = 1.5U_{eq}(C).

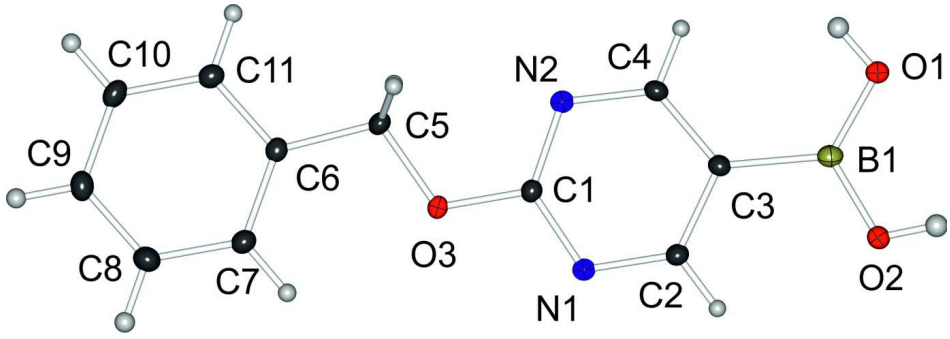


Figure 1

Labelling of atoms and estimation of their atomic thermal motion as Anisotropic Displacement Parameters (ADPs, 50% probability level) for **1**.

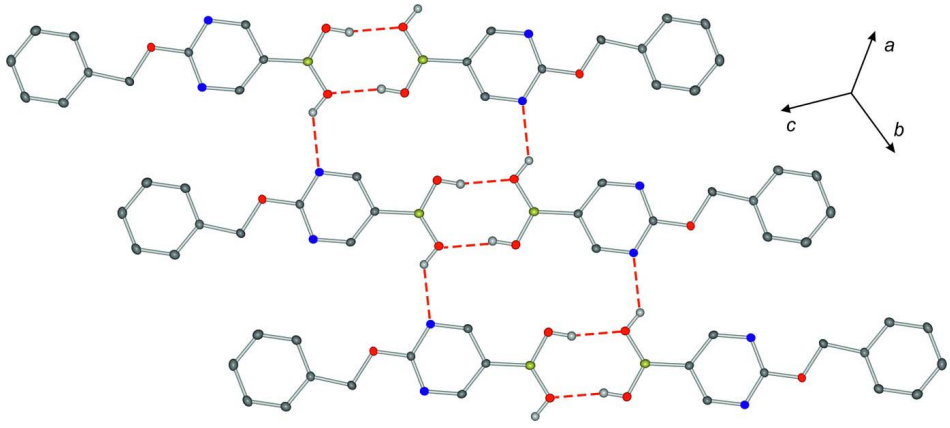


Figure 2

The molecular chains in **1**. Hydrogen bonds are shown as red, dashed lines. Aromatic and aliphatic hydrogen atoms are omitted for clarity.

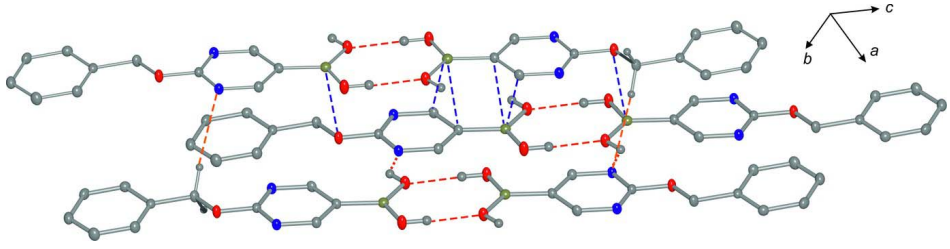


Figure 3

Structural graph displaying the intermolecular O···B, C(π)···B (blue), C—H···N (orange) and O—H···O, O—H···N (red) interactions.

(2-Benzyloxypyrimidin-5-yl)boronic acid

Crystal data

$C_{11}H_{11}BN_2O_3$
M_r = 230.03
Monoclinic, $P2_1/n$
a = 5.498 (1) Å
b = 30.4320 (17) Å
c = 6.7086 (19) Å
β = 113.54 (4)°
V = 1029.0 (4) Å^3

$Z = 4$
$F(000) = 480$
$D_x = 1.485$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 4979 reflections
$\theta = 2.0$–$34.4°$
$\mu = 0.11$ mm^{-1}
$T = 100$ K
Unspecified, colourless
0.20 × 0.15 × 0.15 mm

Data collection

Kuma KM-4 CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
ω scan
Absorption correction: multi-scan (*CrysAlis PRO*; Agilent, 2013)
$T_{min} = 0.993$, $T_{max} = 1.000$
18472 measured reflections
4167 independent reflections
2975 reflections with $I > 2\sigma(I)$
$R_{int} = 0.044$
$\theta_{max} = 34.5°$, $\theta_{min} = 2.7°$
$h = -8 \rightarrow 8$
$k = -48 \rightarrow 47$
$l = -10 \rightarrow 10$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.053$
$wR(F^2) = 0.135$
$S = 1.03$
4167 reflections
160 parameters
0 restraints
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0561P)^2 + 0.4141P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.57$ e Å^{-3}
$\Delta\rho_{min} = -0.30$ e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s 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 (Å^2)

	x	y	z	U_{iso}*/U_{eq}
C1	0.7668 (2)	0.09979 (4)	0.33931 (19)	0.0119 (2)
C2	0.4044 (2)	0.05846 (4)	0.16000 (19)	0.0129 (2)
H2	0.2541	0.0426	0.1570	0.016*
C3	0.4464 (2)	0.06065 (4)	−0.03164 (19)	0.0120 (2)
C4	0.6720 (2)	0.08390 (4)	−0.01318 (19)	0.0135 (2)
H4	0.7143	0.0856	−0.1371	0.016*
C5	1.1273 (2)	0.14700 (4)	0.5176 (2)	0.0144 (2)
H5A	1.0515	0.1694	0.4023	0.017*
H5B	1.2516	0.1286	0.4803	0.017*
C6	1.2746 (2)	0.16928 (4)	0.73226 (19)	0.0119 (2)
C7	1.1923 (2)	0.16861 (4)	0.9030 (2)	0.0152 (2)
H7	1.0405	0.1521	0.8908	0.018*
C8	1.3326 (3)	0.19224 (4)	1.0918 (2)	0.0178 (2)

H8	1.2757	0.1916	1.2081	0.021*
C9	1.5544 (3)	0.21671 (4)	1.1128 (2)	0.0170 (2)
H9	1.6466	0.2333	1.2410	0.020*
C10	1.6401 (3)	0.21665 (4)	0.9434 (2)	0.0161 (2)
H10	1.7933	0.2329	0.9567	0.019*
C11	1.5022 (2)	0.19294 (4)	0.7556 (2)	0.0143 (2)
H11	1.5630	0.1928	0.6415	0.017*
B1	0.2490 (3)	0.03690 (4)	−0.2435 (2)	0.0129 (2)
N1	0.5624 (2)	0.07726 (3)	0.34800 (16)	0.0133 (2)
N2	0.8334 (2)	0.10406 (4)	0.16971 (17)	0.0137 (2)
O1	0.28595 (18)	0.03484 (3)	−0.43207 (14)	0.01608 (19)
O2	0.03654 (19)	0.01745 (3)	−0.22897 (15)	0.0177 (2)
O3	0.91719 (17)	0.11992 (3)	0.52723 (14)	0.01468 (18)
H1A	0.416 (3)	0.0477 (6)	−0.445 (3)	0.022*
H2A	−0.068 (3)	0.0034 (6)	−0.340 (3)	0.022*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0114 (5)	0.0120 (5)	0.0124 (5)	−0.0016 (4)	0.0048 (4)	−0.0011 (4)
C2	0.0135 (5)	0.0138 (5)	0.0122 (5)	−0.0028 (4)	0.0059 (4)	−0.0002 (4)
C3	0.0129 (5)	0.0125 (5)	0.0112 (5)	−0.0013 (4)	0.0054 (4)	−0.0001 (4)
C4	0.0150 (5)	0.0157 (5)	0.0119 (5)	−0.0016 (4)	0.0074 (4)	−0.0008 (4)
C5	0.0134 (5)	0.0163 (5)	0.0144 (5)	−0.0052 (4)	0.0066 (4)	−0.0024 (4)
C6	0.0112 (5)	0.0111 (5)	0.0128 (5)	−0.0006 (4)	0.0039 (4)	−0.0003 (4)
C7	0.0145 (5)	0.0163 (5)	0.0159 (5)	−0.0030 (4)	0.0073 (5)	−0.0007 (4)
C8	0.0201 (6)	0.0202 (6)	0.0149 (5)	−0.0038 (5)	0.0088 (5)	−0.0018 (5)
C9	0.0167 (6)	0.0169 (6)	0.0152 (5)	−0.0021 (4)	0.0040 (5)	−0.0029 (4)
C10	0.0121 (5)	0.0165 (6)	0.0183 (6)	−0.0027 (4)	0.0046 (5)	−0.0012 (4)
C11	0.0136 (5)	0.0149 (5)	0.0153 (5)	−0.0008 (4)	0.0067 (4)	0.0002 (4)
B1	0.0134 (6)	0.0125 (6)	0.0133 (6)	0.0003 (4)	0.0060 (5)	0.0019 (5)
N1	0.0130 (5)	0.0154 (5)	0.0119 (4)	−0.0033 (4)	0.0054 (4)	−0.0013 (4)
N2	0.0141 (5)	0.0157 (5)	0.0125 (4)	−0.0035 (4)	0.0064 (4)	−0.0016 (4)
O1	0.0171 (4)	0.0204 (4)	0.0126 (4)	−0.0069 (3)	0.0079 (3)	−0.0029 (3)
O2	0.0179 (4)	0.0240 (5)	0.0124 (4)	−0.0093 (4)	0.0071 (3)	−0.0041 (4)
O3	0.0148 (4)	0.0175 (4)	0.0121 (4)	−0.0069 (3)	0.0057 (3)	−0.0036 (3)

Geometric parameters (Å, º)

C1—N2	1.3336 (15)	C6—C11	1.3972 (16)
C1—N1	1.3375 (15)	C7—C8	1.3912 (18)
C1—O3	1.3474 (15)	C7—H7	0.9500
C2—N1	1.3407 (16)	C8—C9	1.3870 (18)
C2—C3	1.3957 (17)	C8—H8	0.9500
C2—H2	0.9500	C9—C10	1.3933 (19)
C3—C4	1.3898 (16)	C9—H9	0.9500
C3—B1	1.5775 (19)	C10—C11	1.3856 (18)
C4—N2	1.3415 (16)	C10—H10	0.9500

C4—H4	0.9500	C11—H11	0.9500
C5—O3	1.4412 (14)	B1—O2	1.3475 (16)
C5—C6	1.5028 (18)	B1—O1	1.3602 (16)
C5—H5A	0.9900	O1—H1A	0.849 (18)
C5—H5B	0.9900	O2—H2A	0.852 (19)
C6—C7	1.3898 (17)		

N2—C1—N1	127.51 (11)	C6—C7—H7	120.1
N2—C1—O3	118.63 (10)	C8—C7—H7	120.1
N1—C1—O3	113.86 (10)	C9—C8—C7	121.03 (12)
N1—C2—C3	124.24 (11)	C9—C8—H8	119.5
N1—C2—H2	117.9	C7—C8—H8	119.5
C3—C2—H2	117.9	C8—C9—C10	119.09 (12)
C4—C3—C2	114.36 (11)	C8—C9—H9	120.5
C4—C3—B1	125.58 (11)	C10—C9—H9	120.5
C2—C3—B1	120.05 (10)	C11—C10—C9	120.12 (12)
N2—C4—C3	123.72 (11)	C11—C10—H10	119.9
N2—C4—H4	118.1	C9—C10—H10	119.9
C3—C4—H4	118.1	C10—C11—C6	120.71 (12)
O3—C5—C6	110.46 (10)	C10—C11—H11	119.6
O3—C5—H5A	109.6	C6—C11—H11	119.6
C6—C5—H5A	109.6	O2—B1—O1	120.19 (12)
O3—C5—H5B	109.6	O2—B1—C3	116.12 (11)
C6—C5—H5B	109.6	O1—B1—C3	123.67 (11)
H5A—C5—H5B	108.1	C1—N1—C2	114.70 (10)
C7—C6—C11	119.14 (11)	C1—N2—C4	115.40 (10)
C7—C6—C5	123.72 (11)	B1—O1—H1A	121.3 (12)
C11—C6—C5	117.11 (11)	B1—O2—H2A	117.4 (12)
C6—C7—C8	119.86 (11)	C1—O3—C5	114.90 (9)

N1—C2—C3—C4	0.78 (18)	C4—C3—B1—O2	−177.72 (12)
N1—C2—C3—B1	179.43 (11)	C2—C3—B1—O2	3.78 (17)
C2—C3—C4—N2	−2.18 (18)	C4—C3—B1—O1	3.3 (2)
B1—C3—C4—N2	179.25 (12)	C2—C3—B1—O1	−175.21 (12)
O3—C5—C6—C7	−8.77 (17)	N2—C1—N1—C2	−2.59 (19)
O3—C5—C6—C11	173.27 (10)	O3—C1—N1—C2	177.44 (10)
C11—C6—C7—C8	1.58 (19)	C3—C2—N1—C1	1.38 (18)
C5—C6—C7—C8	−176.34 (12)	N1—C1—N2—C4	1.33 (19)
C6—C7—C8—C9	0.2 (2)	O3—C1—N2—C4	−178.69 (11)
C7—C8—C9—C10	−1.5 (2)	C3—C4—N2—C1	1.25 (18)
C8—C9—C10—C11	0.98 (19)	N2—C1—O3—C5	4.30 (16)
C9—C10—C11—C6	0.78 (19)	N1—C1—O3—C5	−175.72 (10)
C7—C6—C11—C10	−2.06 (18)	C6—C5—O3—C1	177.64 (10)
C5—C6—C11—C10	176.00 (11)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C2—H2···O2^{i}	0.95	2.60	3.5104 (15)	161
O2—H2*A*···O1^{ii}	0.852 (19)	1.915 (19)	2.7615 (16)	172.7 (17)
O1—H1*A*···N1^{iii}	0.849 (18)	2.067 (18)	2.8188 (15)	147.2 (16)

Symmetry codes: (i) −*x*, −*y*, −*z*; (ii) −*x*, −*y*, −*z*−1; (iii) *x*, *y*, *z*−1.