

Acta Crystallographica Section E

Structure Reports

Online

ISSN 1600-5368

2-(3-Methoxyphenyl)-1,3-dihydro-1,3,2-benzodiazaborole

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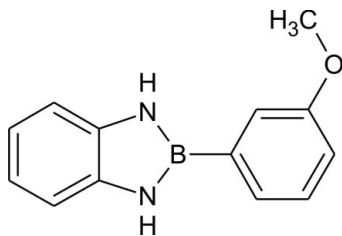
Received 18 June 2012; accepted 22 June 2012

 Key indicators: single-crystal X-ray study; $T = 110$ K; mean $\sigma(\text{C}-\text{C}) = 0.002$ Å; R factor = 0.034; wR factor = 0.094; data-to-parameter ratio = 13.0.

The title compound, $\text{C}_{13}\text{H}_{13}\text{BN}_2\text{O}$, is one in a series of 1,3,2-benzodiazaboroles featuring a 2-methoxyphenyl substitution at the 2-position in the nitrogen–boron heterocycle. The dihedral angle between the mean planes of the benzodiazaborole and 2-methoxyphenyl ring systems is $21.5(1)^\circ$. There is an intermolecular hydrogen bond between one of the NH groups and the methoxy O atom. This hydrogen bond leads to an infinite hydrogen-bonded chain colinear with the a axis.

Related literature

For the synthesis of the title compound, see: Sithebe *et al.* (2011); Weber *et al.* (2009, 2011). For related derivatives as well as their photoluminescence studies, see: Weber *et al.* (2010); Maruyama & Kawanishi (2002). For structures of related compounds, see: Slabber *et al.* (2011); Akerman *et al.* (2011). For applications of 1,3,2-diazaborolyl compounds, see: Schwedler *et al.* (2011).



Experimental

Crystal data

 $\text{C}_{13}\text{H}_{13}\text{BN}_2\text{O}$
 $M_r = 224.06$

 Orthorhombic, $P2_12_12_1$
 $a = 7.549(5)$ Å

 $b = 12.230(5)$ Å

 $c = 12.308(5)$ Å

 $V = 1136.3(10)$ Å³
 $Z = 4$

 Mo $K\alpha$ radiation

 $\mu = 0.08$ mm⁻¹
 $T = 110$ K

 $0.50 \times 0.40 \times 0.40$ mm

Data collection

Oxford Diffraction Xcalibur 2 CCD diffractometer

Absorption correction: multi-scan (Blessing, 1995)

 $T_{\min} = 0.960$, $T_{\max} = 0.968$

11586 measured reflections

2125 independent reflections

 1939 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.031$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.034$
 $wR(F^2) = 0.094$
 $S = 1.05$

2125 reflections

164 parameters

H atoms treated by a mixture of independent and constrained refinement

 $\Delta\rho_{\max} = 0.32$ e Å⁻³
 $\Delta\rho_{\min} = -0.20$ e Å⁻³
Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{N2}-\text{H102}\cdots\text{O001}^i$	0.89 (2)	2.40 (2)	3.201 (2)	151 (2)

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

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2008); cell refinement: *CrysAlis CCD*; data reduction: *CrysAlis RED* (Oxford Diffraction, 2008); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *Mercury* (Macrae *et al.*, 2006) and *POV-RAY* (Cason *et al.*, 2002); software used to prepare material for publication: *publCIF* (Westrip, 2010).

We gratefully acknowledge the National Research Foundation and the University of KwaZulu Natal for financial assistance.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: NK2170).

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supporting information

Acta Cryst. (2012). E68, o2241 [https://doi.org/10.1107/S1600536812028437]

2-(3-Methoxyphenyl)-1,3-dihydro-1,3,2-benzodiazaborole**Ross S. Robinson, Siphamandla Sithebe and Matthew P. Akerman****S1. Comment**

Molecular compounds functionalized with 1,3,2-diazaborolyl groups have received considerable attention and have been investigated for their optical, electronic and ion sensing abilities, making them possible candidates for use in advanced material science (Schwedler *et al.*, 2011). Rapid developments in the chemistry of 1,3,2-diazaborolyl containing compounds, due to their photoluminescence characteristics and unusual stability, have been observed in recent years. Unlike most triarylborane compounds which require dimesitylborolyl moieties for the enhancement of their stability, 2-arylbenzo-1,3,2-diazaborole compounds have been reported to be water and air stable without any additional dimesityl groups (Weber *et al.*, 2009). To gain insight into the intriguing characteristics exhibited by these compounds, we (Sithebe *et al.*, 2011) and other researchers (Maruyama *et al.*, 2002 and Weber *et al.* 2011) have directed our research focus towards the investigation of the photophysical studies as well as the determination of the crystal structures of 1,3,2-benzodiazaborolyl compounds.

The molecule features a 1,3,2-benzodiazaborolyl backbone with a five-membered diazaborole ring substituted with hydrogen atoms at the 1- and 3-positions, and a 3-methoxyphenyl ring at the 2-position. The 1,3,2-benzodiazaborolyl backbone of the molecule is essentially planar, however, the 3-methoxyphenyl ring at the 2-position, is rotated out of plane with a dihedral angle of 21.5 (1)°. The two N—B bonds are approximately equal (averaged to 1.433 (2) Å). The N1—B—N2 bond angle is 105.2 (1)°, the N1—B—C1 and N2—B—C1 bond angles are slightly different, measuring 125.4 (1)° and 129.3 (1)°, respectively (refer to Figure 1 for the atom numbering scheme). These bond lengths and angles compare favourably to those of previously reported diazaborolyl systems (Weber *et al.*, 2009). The molecules are linked through hydrogen bonding forming infinite, one-dimensional chains co-linear with the *a*-axis (Figure 2). The amine NH acts as the hydrogen bond donor and the etheryl oxygen atom the H-bond acceptor. The hydrogen bond lengths and bond angles are summarized in Table 1.

S2. Experimental

3-Methoxyphenylboronic acid (1.00 g, 5.18 mmol) and *o*-phenylenediamine (0.56 g, 5.18 mmol) were dissolved in toluene (80 ml) in a two neck flask equipped with a Dean and Stark Apparatus, magnetic stirrer bar and reflux condenser. The mixture was heated under reflux overnight and the solvent was removed *in vacuo*, affording 2-{3-methoxyphenyl}-benzo-1,3,2-diazaborole as an off-white solid. The desired product was purified using a flash column and radial chromatography using Hexane: Ethyl acetate (8:2) as the eluent. Crystals suitable for X-ray diffraction were grown by slow evaporation of a *n*-hexane:dichloromethane (6:4) solution.

S3. Refinement

All non-hydrogen atoms were located in the difference Fourier map and refined anisotropically. The positions of all hydrogen atoms were calculated using the standard riding model of *SHELXL97*. with C—H(aromatic) distances of 0.93 Å

and $U_{\text{iso}} = 1.2 U_{\text{eq}}$, and C—H(methyl) distances of 0.96 Å and $U_{\text{iso}} = 1.5 U_{\text{eq}}$. The amine hydrogen atoms were located in the difference Fourier map and allowed to refine isotropically. In the absence of significant anomalous scattering, Friedel pairs were merged.

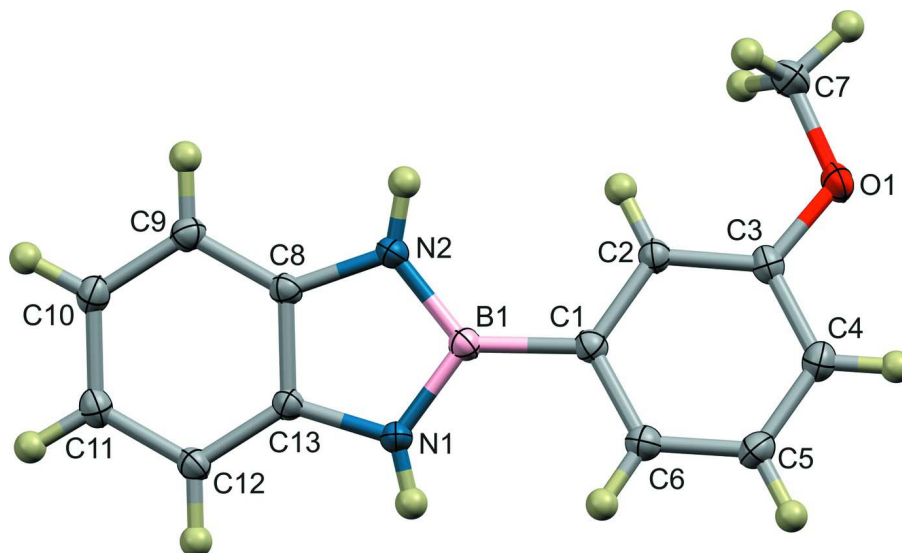


Figure 1
Displacement ellipsoid plot of (1) at the 50% probability level.

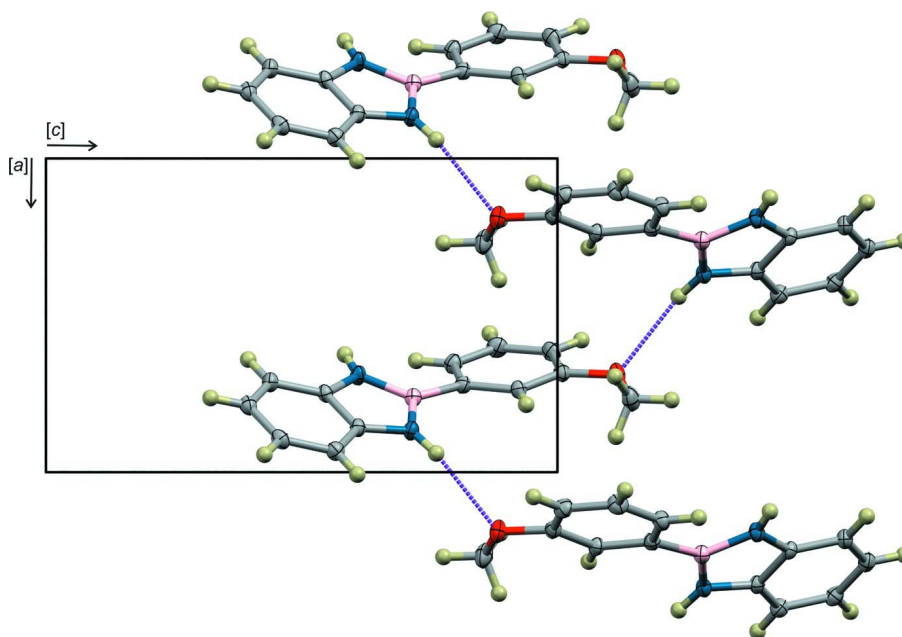


Figure 2
Hydrogen bonding interactions in (1), shown as dashed lines, viewed down the *b*-axis.

2-(3-Methoxyphenyl)-1,3-dihydro-1,3,2-benzodiazaborole

Crystal data

C₁₃H₁₃BN₂O $M_r = 224.06$ Orthorhombic, $P2_12_12_1$

Hall symbol: P 2ac 2ab

 $a = 7.549 (5) \text{ \AA}$ $b = 12.230 (5) \text{ \AA}$ $c = 12.308 (5) \text{ \AA}$ $V = 1136.3 (10) \text{ \AA}^3$ $Z = 4$ $F(000) = 472$ $D_x = 1.310 \text{ Mg m}^{-3}$ Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$

Cell parameters from 1939 reflections

 $\theta = 3.2\text{--}32.1^\circ$ $\mu = 0.08 \text{ mm}^{-1}$ $T = 110 \text{ K}$

Needle, colourless

 $0.50 \times 0.40 \times 0.40 \text{ mm}$

Data collection

Oxford Diffraction Xcalibur 2 CCD
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

 ω scans at fixed θ anglesAbsorption correction: multi-scan
(Blessing, 1995) $T_{\min} = 0.960$, $T_{\max} = 0.968$

11586 measured reflections

2125 independent reflections

1939 reflections with $I > 2\sigma(I)$ $R_{\text{int}} = 0.031$ $\theta_{\max} = 32.1^\circ$, $\theta_{\min} = 3.2^\circ$ $h = -11 \rightarrow 7$ $k = -17 \rightarrow 18$ $l = -18 \rightarrow 18$

Refinement

Refinement on F^2

Least-squares matrix: full

 $R[F^2 > 2\sigma(F^2)] = 0.034$ $wR(F^2) = 0.094$ $S = 1.05$

2125 reflections

164 parameters

0 restraints

Primary atom site location: structure-invariant
direct methodsSecondary atom site location: difference Fourier
mapHydrogen site location: inferred from
neighbouring sitesH atoms treated by a mixture of independent
and constrained refinement $w = 1/[\sigma^2(F_o^2) + (0.0725P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\max} < 0.001$ $\Delta\rho_{\max} = 0.32 \text{ e \AA}^{-3}$ $\Delta\rho_{\min} = -0.20 \text{ e \AA}^{-3}$ Extinction correction: *SHELXL97* (Sheldrick,
2008), $F_c^* = kFc[1 + 0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$

Extinction coefficient: 0.058 (6)

Special details

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

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
O001	0.68887 (13)	0.34747 (7)	1.11670 (7)	0.0238 (2)
N2	0.86812 (15)	0.17066 (8)	0.71418 (8)	0.0184 (2)
N1	0.69146 (14)	0.27984 (8)	0.61068 (8)	0.0187 (2)

C8	0.85853 (16)	0.12575 (9)	0.61012 (9)	0.0171 (2)
C2	0.73726 (16)	0.30830 (10)	0.92377 (10)	0.0179 (2)
H2	0.7848	0.2380	0.9388	0.022*
C6	0.65474 (16)	0.44957 (10)	0.79625 (10)	0.0217 (2)
H6	0.6449	0.4756	0.7238	0.026*
C11	0.78716 (17)	0.07371 (10)	0.39528 (10)	0.0208 (2)
H11	0.7634	0.0544	0.3219	0.025*
C13	0.74943 (16)	0.19384 (9)	0.54613 (9)	0.0168 (2)
C12	0.71345 (16)	0.16880 (10)	0.43846 (9)	0.0194 (2)
H12	0.6407	0.2151	0.3954	0.023*
C1	0.72155 (16)	0.34445 (10)	0.81557 (9)	0.0181 (2)
C9	0.93295 (17)	0.03188 (10)	0.56632 (11)	0.0203 (2)
H9	1.0075	-0.0139	0.6087	0.024*
C4	0.61570 (17)	0.47951 (10)	0.98828 (10)	0.0228 (3)
H4	0.5789	0.5249	1.0467	0.027*
C3	0.68309 (17)	0.37557 (10)	1.00871 (10)	0.0193 (2)
C5	0.60273 (18)	0.51624 (10)	0.88201 (11)	0.0241 (3)
H5	0.5580	0.5874	0.8677	0.029*
C10	0.89523 (17)	0.00661 (10)	0.45839 (10)	0.0213 (2)
H10	0.9442	-0.0577	0.4272	0.026*
C7	0.7662 (2)	0.24408 (11)	1.14365 (11)	0.0296 (3)
H7A	0.6947	0.1852	1.1122	0.044*
H7B	0.7700	0.2358	1.2228	0.044*
H7C	0.8868	0.2405	1.1144	0.044*
B1	0.76235 (18)	0.26817 (10)	0.71788 (10)	0.0179 (2)
H102	0.940 (3)	0.1411 (15)	0.7630 (17)	0.042 (5)*
H101	0.625 (3)	0.3271 (17)	0.5846 (18)	0.050 (6)*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O001	0.0320 (5)	0.0242 (4)	0.0153 (4)	0.0015 (4)	0.0037 (4)	-0.0013 (3)
N2	0.0218 (5)	0.0184 (4)	0.0150 (4)	0.0016 (4)	-0.0021 (4)	0.0006 (3)
N1	0.0233 (5)	0.0172 (4)	0.0156 (4)	0.0040 (4)	-0.0009 (4)	0.0001 (4)
C8	0.0195 (5)	0.0166 (5)	0.0152 (5)	-0.0009 (4)	0.0005 (4)	0.0018 (4)
C2	0.0197 (5)	0.0175 (5)	0.0166 (5)	-0.0002 (4)	0.0004 (4)	-0.0011 (4)
C6	0.0237 (6)	0.0211 (5)	0.0202 (5)	0.0015 (5)	-0.0015 (5)	0.0007 (4)
C11	0.0239 (6)	0.0214 (5)	0.0172 (5)	-0.0029 (5)	0.0019 (5)	-0.0017 (4)
C13	0.0196 (5)	0.0158 (4)	0.0150 (5)	0.0004 (4)	0.0013 (4)	0.0009 (4)
C12	0.0224 (5)	0.0207 (5)	0.0151 (5)	0.0000 (4)	-0.0003 (4)	0.0006 (4)
C1	0.0188 (5)	0.0185 (5)	0.0170 (5)	-0.0006 (4)	-0.0008 (4)	-0.0006 (4)
C9	0.0219 (5)	0.0182 (5)	0.0207 (5)	0.0018 (4)	0.0015 (5)	0.0018 (4)
C4	0.0243 (6)	0.0220 (6)	0.0221 (6)	0.0024 (5)	0.0021 (5)	-0.0036 (4)
C3	0.0202 (5)	0.0210 (5)	0.0166 (5)	-0.0022 (4)	0.0010 (4)	-0.0020 (4)
C5	0.0265 (6)	0.0194 (5)	0.0265 (6)	0.0047 (5)	-0.0011 (5)	-0.0010 (5)
C10	0.0242 (6)	0.0180 (5)	0.0219 (5)	0.0004 (5)	0.0041 (5)	-0.0015 (4)
C7	0.0382 (7)	0.0313 (7)	0.0195 (5)	0.0066 (6)	0.0031 (5)	0.0052 (5)
B1	0.0202 (5)	0.0178 (5)	0.0157 (5)	-0.0005 (5)	0.0001 (5)	0.0003 (4)

Geometric parameters (Å, °)

O001—C3	1.3735 (15)	C11—C10	1.3937 (18)
O001—C7	1.4316 (17)	C11—C12	1.3945 (17)
N2—C8	1.3954 (15)	C11—H11	0.9500
N2—B1	1.4359 (17)	C13—C12	1.3870 (16)
N2—H102	0.89 (2)	C12—H12	0.9500
N1—C13	1.3888 (15)	C1—B1	1.5527 (18)
N1—B1	1.4309 (17)	C9—C10	1.3933 (19)
N1—H101	0.83 (2)	C9—H9	0.9500
C8—C9	1.3872 (17)	C4—C5	1.3864 (19)
C8—C13	1.4115 (16)	C4—C3	1.3921 (18)
C2—C3	1.3918 (16)	C4—H4	0.9500
C2—C1	1.4081 (17)	C5—H5	0.9500
C2—H2	0.9500	C10—H10	0.9500
C6—C5	1.3903 (18)	C7—H7A	0.9800
C6—C1	1.4013 (17)	C7—H7B	0.9800
C6—H6	0.9500	C7—H7C	0.9800
C3—O001—C7	117.27 (10)	C6—C1—B1	119.42 (11)
C8—N2—B1	109.10 (10)	C2—C1—B1	121.80 (11)
C8—N2—H102	119.5 (12)	C8—C9—C10	118.12 (12)
B1—N2—H102	131.1 (12)	C8—C9—H9	120.9
C13—N1—B1	109.52 (10)	C10—C9—H9	120.9
C13—N1—H101	119.8 (15)	C5—C4—C3	119.48 (12)
B1—N1—H101	130.7 (15)	C5—C4—H4	120.3
C9—C8—N2	131.41 (11)	C3—C4—H4	120.3
C9—C8—C13	120.51 (11)	O001—C3—C2	124.73 (11)
N2—C8—C13	108.07 (10)	O001—C3—C4	114.51 (11)
C3—C2—C1	120.01 (11)	C2—C3—C4	120.76 (12)
C3—C2—H2	120.0	C4—C5—C6	120.41 (12)
C1—C2—H2	120.0	C4—C5—H5	119.8
C5—C6—C1	120.72 (12)	C6—C5—H5	119.8
C5—C6—H6	119.6	C9—C10—C11	121.36 (12)
C1—C6—H6	119.6	C9—C10—H10	119.3
C10—C11—C12	120.81 (12)	C11—C10—H10	119.3
C10—C11—H11	119.6	O001—C7—H7A	109.5
C12—C11—H11	119.6	O001—C7—H7B	109.5
C12—C13—N1	130.70 (11)	H7A—C7—H7B	109.5
C12—C13—C8	121.14 (11)	O001—C7—H7C	109.5
N1—C13—C8	108.15 (10)	H7A—C7—H7C	109.5
C13—C12—C11	118.05 (12)	H7B—C7—H7C	109.5
C13—C12—H12	121.0	N1—B1—N2	105.16 (10)
C11—C12—H12	121.0	N1—B1—C1	125.44 (11)
C6—C1—C2	118.61 (11)	N2—B1—C1	129.33 (11)
B1—N2—C8—C9	-178.52 (13)	C7—O001—C3—C4	-176.53 (12)
B1—N2—C8—C13	0.68 (13)	C1—C2—C3—O001	178.47 (12)

B1—N1—C13—C12	178.50 (13)	C1—C2—C3—C4	-1.02 (18)
B1—N1—C13—C8	-0.17 (14)	C5—C4—C3—O001	-179.61 (12)
C9—C8—C13—C12	0.17 (18)	C5—C4—C3—C2	-0.07 (19)
N2—C8—C13—C12	-179.14 (11)	C3—C4—C5—C6	0.7 (2)
C9—C8—C13—N1	178.99 (10)	C1—C6—C5—C4	-0.2 (2)
N2—C8—C13—N1	-0.32 (13)	C8—C9—C10—C11	0.53 (18)
N1—C13—C12—C11	-178.02 (12)	C12—C11—C10—C9	0.14 (19)
C8—C13—C12—C11	0.50 (18)	C13—N1—B1—N2	0.57 (13)
C10—C11—C12—C13	-0.65 (18)	C13—N1—B1—C1	-176.89 (11)
C5—C6—C1—C2	-0.88 (19)	C8—N2—B1—N1	-0.76 (13)
C5—C6—C1—B1	174.46 (12)	C8—N2—B1—C1	176.55 (12)
C3—C2—C1—C6	1.48 (18)	C6—C1—B1—N1	-19.86 (19)
C3—C2—C1—B1	-173.75 (12)	C2—C1—B1—N1	155.33 (12)
N2—C8—C9—C10	178.44 (12)	C6—C1—B1—N2	163.32 (12)
C13—C8—C9—C10	-0.68 (17)	C2—C1—B1—N2	-21.5 (2)
C7—O001—C3—C2	3.95 (18)		

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>
N2—H102 \cdots O001 ⁱ	0.89 (2)	2.40 (2)	3.201 (2)	151 (2)

Symmetry code: (i) $x+1/2, -y+1/2, -z+2$.