

A co-crystal of 1,10-phenanthroline with boric acid: a novel aza-aromatic complex

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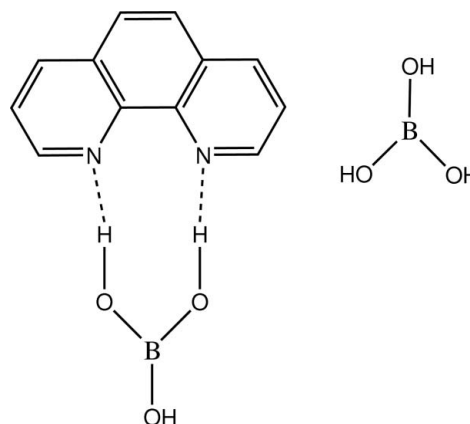
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Key indicators: single-crystal X-ray study; $T = 295$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å; R factor = 0.036; wR factor = 0.096; data-to-parameter ratio = 13.0.

The title compound, $\text{C}_{12}\text{H}_8\text{N}_2 \cdot 2\text{B}(\text{OH})_3$, is best described as a host-guest complex in which the $\text{B}(\text{OH})_3$ molecules form a hydrogen-bonded cyclic network of layers parallel to the ab plane into which the 1,10-phenanthroline molecules are bound. An extensive network of hydrogen bonds are responsible for the crystal stability. No π -stacking interactions occur between the 1,10-phenanthroline molecules.

Related literature

For the design and synthesis of novel systems of non-covalent hosts involving hydrogen bonds, see: Pedireddi *et al.* (1997). In the field of supermolecular synthesis, recognition between the complementary functional groups is a main factor for the evaluation of influence of noncovalent interactions in the formation of specific architecture, see: Lehn (1990). The ability of the $-\text{B}(\text{OH})_2$ functionality to form a variety of hydrogen bonds through different conformations makes it a very suitable moiety for the synthesis of novel molecular complexes, see: Lee *et al.* (2005). It is known to have an affinity for pyridyl N atoms, often forming $\text{O}-\text{H} \cdots \text{N}$ hydrogen bonds, as observed in some crystals of boronic acids with aza compounds (Talwelkar & Pedireddi, 2010). Non-covalent hosts are generally designed and synthesized by employing appropriate functional groups at required symmetry positions to form a cyclic network through the hydrogen bonds, see: Pedireddi (2001). This effect has been observed in simple molecular adducts such as 1,10-phenanthroline and water (Tian *et al.*, 1995).



Experimental

Crystal data

$\text{C}_{12}\text{H}_8\text{N}_2 \cdot 2\text{B}(\text{OH})_3$
 $M_r = 303.87$
 Triclinic, $P\bar{1}$
 $a = 7.1390$ (13) Å
 $b = 9.6189$ (13) Å
 $c = 10.4756$ (15) Å
 $\alpha = 93.767$ (11)°
 $\beta = 101.546$ (14)°

$\gamma = 90.644$ (13)°
 $V = 703.05$ (19) Å³
 $Z = 2$
 Mo $K\alpha$ radiation
 $\mu = 0.11$ mm⁻¹
 $T = 295$ K
 $0.35 \times 0.16 \times 0.09$ mm

Data collection

Oxford Diffraction Xcalibur Eos diffractometer
 Absorption correction: multi-scan [*CrysAlis PRO* (Oxford Diffraction, 2011) based on Clark

& Reid (1995)]
 $T_{\min} = 0.956$, $T_{\max} = 1.000$
 10473 measured reflections
 2580 independent reflections
 1972 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.023$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.036$
 $wR(F^2) = 0.096$
 $S = 1.02$
 2580 reflections

199 parameters
 H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.17$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.13$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H} \cdots A$	$D-\text{H}$	$\text{H} \cdots A$	$D \cdots A$	$D-\text{H} \cdots A$
$\text{O1}-\text{H1} \cdots \text{N2}$	0.85	1.90	2.7360 (16)	169
$\text{O2}-\text{H2} \cdots \text{N1}$	0.85	1.88	2.7132 (17)	167
$\text{O3}-\text{H3} \cdots \text{O1}^{\text{i}}$	0.85	1.86	2.7076 (15)	177
$\text{O4}-\text{H4} \cdots \text{O3}^{\text{i}}$	0.85	1.89	2.7286 (16)	16
$\text{O5}-\text{H5} \cdots \text{O4}^{\text{ii}}$	0.85	1.89	2.7355 (18)	179
$\text{O6}-\text{H6} \cdots \text{O2}^{\text{iii}}$	0.85	1.95	2.7946 (17)	172

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

Data collection: *CrysAlis PRO* (Oxford Diffraction, 2011); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis PRO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008) and *OLEX2* (Dolomanov *et al.*, 2009); software used to prepare material for publication: *publCIF* (Westrip, 2010).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: EZZ2287).

References

- Clark, R. C. & Reid, J. S. (1995). *Acta Cryst.* **A51**, 887–897.
- Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K. & Puschmann, H. (2009). *J. Appl. Cryst.* **42**, 339–341.
- Lee, S. O., Kariuki, B. M. & Harris, K. D. M. (2005). *New. J. Chem.* **29**, 1266–1271.
- Lehn, J. M. (1990). *Angew. Chem. Int. Ed.* **29**, 1304–1319.
- Oxford Diffraction (2011). *CrysAlis PRO*. Oxford Diffraction Ltd, Yarnton, England.
- Pedireddi, V. R. (2001). *Cryst. Growth Des.* **1**, 383–385.
- Pedireddi, V. R., Chatterjee, S., Ranganathan, A. & Rao, C. N. R. (1997). *J. Am. Chem. Soc.* **119**, 10867–10868.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Talwelkar, M. & Pedireddi, V. R. (2010). *Tetrahedron Lett.* **51**, 6901–6905.
- Tian, Y.-P., Duan, C.-Y., Xu, X.-X. & You, X.-Z. (1995). *Acta Cryst.* **C51**, 2309–2312.
- Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.

supporting information

Acta Cryst. (2013). E69, o1067–o1068 [https://doi.org/10.1107/S1600536813015134]

A co-crystal of 1,10-phenanthroline with boric acid: a novel aza-aromatic complex

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S1. Comment

The design and synthesis of novel systems of noncovalent hosts involving hydrogen bonds is a vast research area in both molecular and supermolecular chemistry, see Pedireddi *et al.* (1997). In the field of supermolecular synthesis, recognition between the complementary functional groups is a main factor for the evaluation of influence of noncovalent interaction in the formation of specific architecture, see: Lehn (1990). In recent times, boric acid derivatives have been well considered to be potential co-crystal formers. In fact, the ability of $\text{B}(\text{OH})_2$ functionality to form a variety of hydrogen bonds through different conformations makes it a very suitable moiety for the synthesis of novel molecular complexes, see Lee *et al.* (2005). The $\text{B}(\text{OH})_2$ moiety is known to have an affinity for pyridyl N-atoms, often forming $\text{O}—\text{H}\cdots\text{N}$ hydrogen bonds, as observed in some crystals of boronic acids with aza compounds, see Talwelkar & Pedireddi (2010).

Non-covalent hosts are generally designed and synthesized by employing appropriate functional groups at required symmetry positions to form a cyclic network through the hydrogen bonds, see Pedireddi (2001). This effect has been observed vividly in simple molecular adduct such as 1,10-phenanthroline and water, see Tian *et al.* (1995). In this complex, a water molecule interacts with a molecule of 1,10-phenanthroline through $\text{O}—\text{H}\cdots\text{N}$ hydrogen bonds and a unique aza-aromatic complex is formed. In the latter, 1,10-phenanthroline could be considered as a host. Herein, we report the crystal structure of boric acid with 1,10-phenanthroline as an aza-donor compound.

As seen in Figure 1, the phen molecule forms a H-bonded adduct *via* two $\text{B}—\text{O}—\text{H}\cdots\text{N}$ interacts from one of the included $\text{B}(\text{OH})_3$ moieties. A strong network of hydrogen bonds among the $\text{B}(\text{OH})_3$ units forms a layered structure with alternating $\text{B}(\text{OH})_3$ and phen layers that reside in the *ab* planes (Figure 2). The $\text{B}(\text{OH})_3$ layers alone can be described as a cyclic network formed by hydrogen bonding interactions as can be seen in Figure 3. There are not any significant π -stacking interactions between the phen molecules.

S2. Experimental

$(\text{CH}_3)_3\text{NBH}_3$ (0.73 g, 10 mmol) and iodine (2.54 g, 5 mmol) were dissolved in toluene (4 ml) and stirred for 30 min. A solution of 1,10-phenanthroline (1.98 g, 10 mmol) in toluene (4 ml) was added, and the mixture refluxed overnight. The solution was cooled to room temperature, during which process orange-brown crystals were formed. The product was recrystallized twice from CH_3CN to obtain analytically pure, red-brown crystalline product.

^1H NMR ($\text{DMSO}-d_6$, 300 MHz): δ_{H} 9.22 (dd, $J = 2.8, 1.6$ Hz, 2H), 8.67 (dd, $J = 6.3, 1.6$ Hz, 2H), 8.14 (s, 2H), 7.93 (q, $J = 4.4$ Hz, 2H), 6.62 (br, 2H); ^{13}C NMR ($\text{DMSO}-d_6$, 100 MHz): δ_{C} 151.67, 146.27, 139.09, 130.58, 128.77, 125.66.

S3. Refinement

H-atoms were placed in calculated positions and allowed to ride during subsequent refinement, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ and C—H distances of 0.93 Å for the aromatic H atoms and with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ and O—H distances of 0.85 Å for

hydroxyl H atoms.

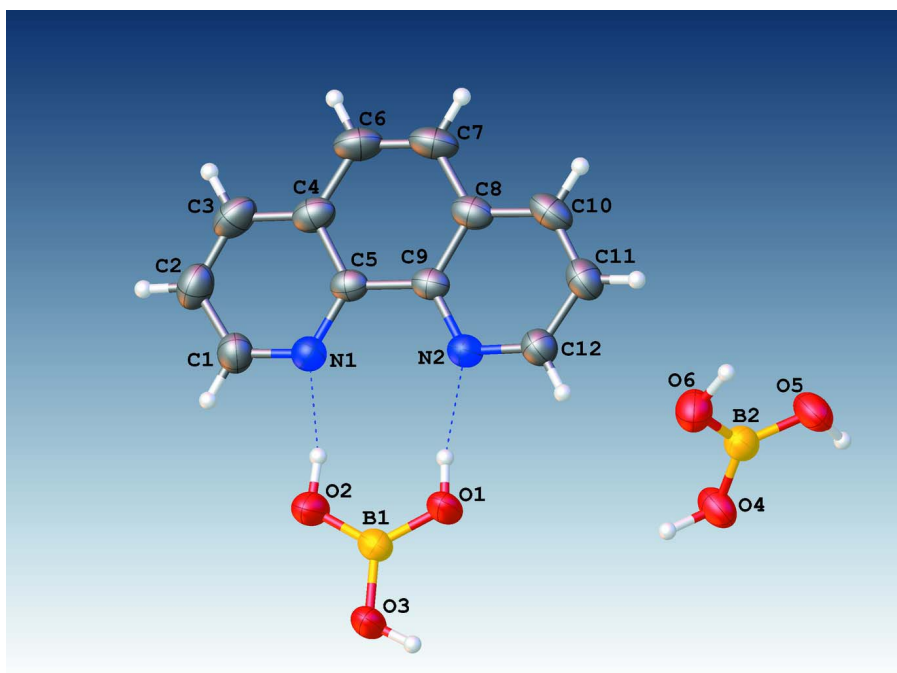


Figure 1

The molecular structure of **I**, with the atom-numbering scheme. Displacement ellipsoids for non-hydrogen atoms are drawn at the 50% probability level.

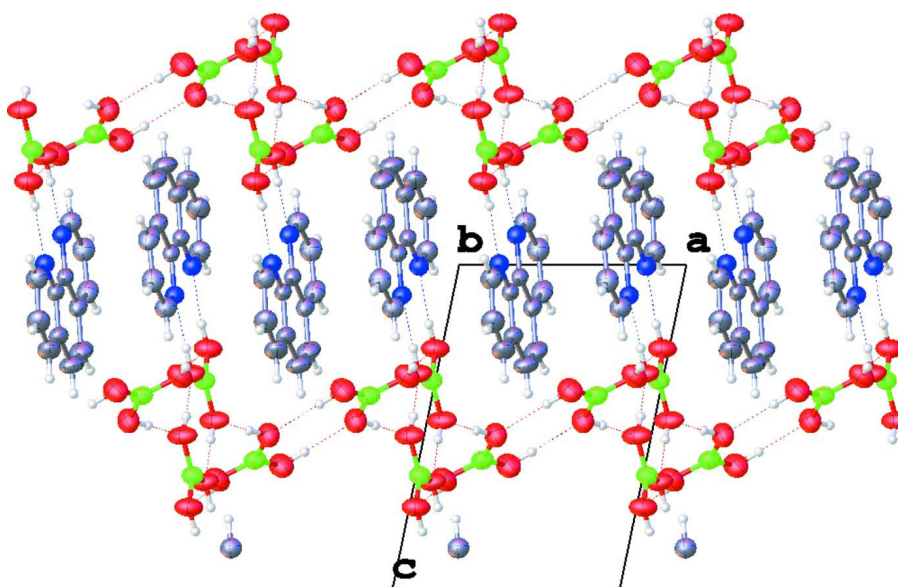


Figure 2

A packing diagram of **I** viewed along the *b* axis.

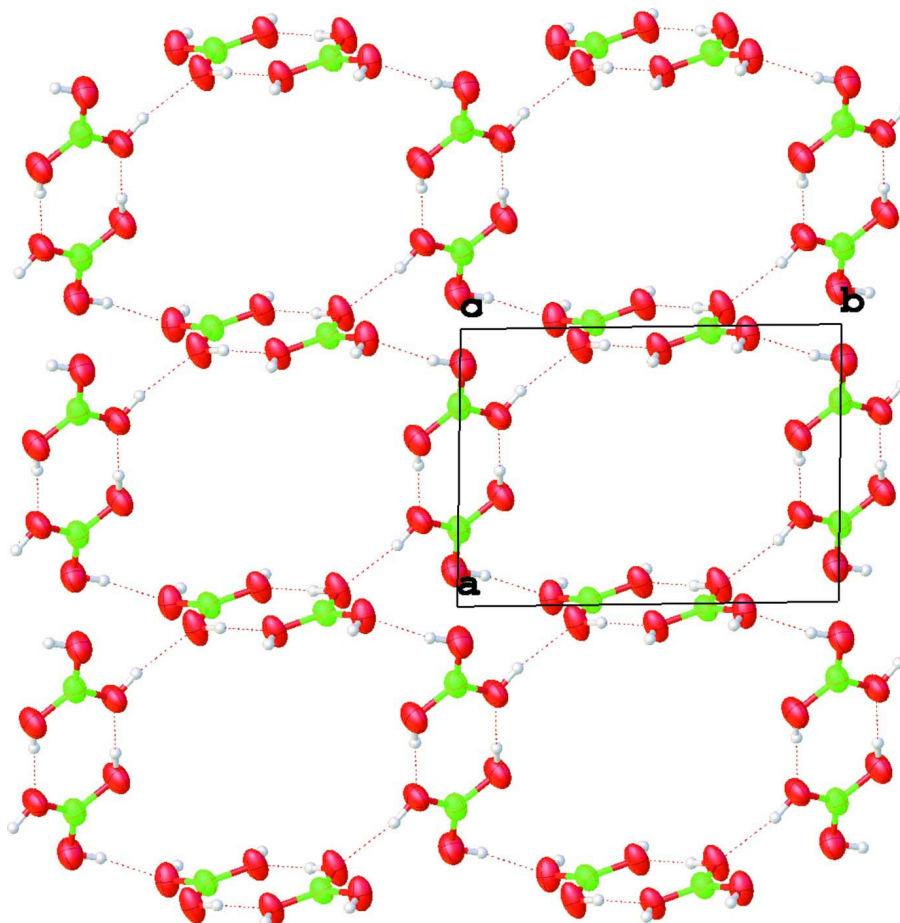


Figure 3

A representation of the two-dimensional B(OH)₃ layers formed *via* hydrogen bonding in the structure of **I**.

Boric acid–1,10-phenanthroline (2/1)

Crystal data

C₁₂H₈N₂·2BH₃O₃

$M_r = 303.87$

Triclinic, $P\bar{1}$

Hall symbol: -P 1

$a = 7.1390$ (13) Å

$b = 9.6189$ (13) Å

$c = 10.4756$ (15) Å

$\alpha = 93.767$ (11)°

$\beta = 101.546$ (14)°

$\gamma = 90.644$ (13)°

$V = 703.05$ (19) Å³

$Z = 2$

$F(000) = 316$

$D_x = 1.435$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 3335 reflections

$\theta = 3.2$ – 25.3 °

$\mu = 0.11$ mm⁻¹

$T = 295$ K

Prism, brown

$0.35 \times 0.16 \times 0.09$ mm

Data collection

Oxford Diffraction Xcalibur Eos
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

Detector resolution: 16.0514 pixels mm⁻¹

ω scans

Absorption correction: multi-scan

[*CrysAlis PRO* (Oxford Diffraction, 2011) based
on Clark & Reid (1995)]

$T_{\min} = 0.956$, $T_{\max} = 1.000$

10473 measured reflections
 2580 independent reflections
 1972 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.023$

$\theta_{\text{max}} = 25.4^\circ$, $\theta_{\text{min}} = 3.2^\circ$
 $h = -8 \rightarrow 8$
 $k = -11 \rightarrow 11$
 $l = -12 \rightarrow 12$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.036$
 $wR(F^2) = 0.096$
 $S = 1.02$
 2580 reflections
 199 parameters
 0 restraints
 Primary atom site location: structure-invariant
 direct methods

Secondary atom site location: difference Fourier
 map
 Hydrogen site location: inferred from
 neighbouring sites
 H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.044P)^2 + 0.1204P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.17 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.13 \text{ e } \text{\AA}^{-3}$

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 $F^2 > 2\sigma(F^2)$ 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	$U_{\text{iso}}^*/U_{\text{eq}}$
B1	0.0170 (3)	0.65229 (18)	0.64598 (18)	0.0421 (4)
B2	0.2786 (3)	-0.00132 (19)	0.59856 (18)	0.0439 (4)
C1	0.1542 (2)	0.83587 (17)	1.04155 (17)	0.0488 (4)
H1A	0.1058	0.9001	0.9816	0.059*
C2	0.1999 (3)	0.8822 (2)	1.17305 (19)	0.0573 (5)
H2A	0.1815	0.9743	1.1999	0.069*
C3	0.2718 (3)	0.7893 (2)	1.26068 (18)	0.0574 (5)
H3A	0.3014	0.8168	1.3493	0.069*
C4	0.3018 (2)	0.65145 (18)	1.21789 (15)	0.0464 (4)
C5	0.2496 (2)	0.61314 (16)	1.08273 (14)	0.0369 (4)
C6	0.3852 (3)	0.5520 (2)	1.30610 (17)	0.0587 (5)
H6A	0.4195	0.5784	1.3948	0.070*
C7	0.4149 (3)	0.4217 (2)	1.26368 (18)	0.0567 (5)
H7	0.4714	0.3593	1.3231	0.068*
C8	0.3612 (2)	0.37654 (17)	1.12795 (16)	0.0434 (4)
C9	0.2778 (2)	0.47095 (15)	1.03670 (14)	0.0361 (3)
C10	0.3890 (2)	0.23972 (17)	1.08186 (18)	0.0521 (5)
H10	0.4451	0.1755	1.1396	0.062*
C11	0.3337 (2)	0.20134 (17)	0.95254 (18)	0.0513 (4)
H11	0.3496	0.1107	0.9206	0.062*
C12	0.2522 (2)	0.30118 (16)	0.86861 (16)	0.0449 (4)

H12	0.2150	0.2741	0.7802	0.054*
N1	0.17492 (17)	0.70652 (13)	0.99611 (12)	0.0403 (3)
N2	0.22495 (17)	0.43158 (12)	0.90711 (12)	0.0385 (3)
O1	0.07961 (17)	0.52138 (11)	0.66548 (10)	0.0515 (3)
H1	0.1261	0.5050	0.7441	0.077*
O2	0.02929 (18)	0.75343 (11)	0.74334 (11)	0.0548 (3)
H2	0.0796	0.7268	0.8180	0.082*
O3	-0.06394 (19)	0.68679 (11)	0.52361 (11)	0.0583 (4)
H3	-0.0642	0.6217	0.4646	0.087*
O4	0.31472 (16)	0.10158 (11)	0.52210 (12)	0.0539 (3)
H4	0.2251	0.1595	0.5081	0.081*
O5	0.39825 (18)	-0.11040 (12)	0.61562 (12)	0.0587 (3)
H5	0.4881	-0.1068	0.5734	0.088*
O6	0.12843 (18)	0.00858 (12)	0.65864 (12)	0.0584 (3)
H6	0.1101	-0.0702	0.6871	0.088*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
B1	0.0496 (11)	0.0403 (10)	0.0372 (10)	0.0098 (8)	0.0080 (8)	0.0079 (8)
B2	0.0530 (12)	0.0390 (10)	0.0376 (10)	0.0063 (8)	0.0042 (9)	0.0014 (8)
C1	0.0501 (10)	0.0455 (10)	0.0492 (10)	0.0076 (7)	0.0074 (8)	-0.0006 (8)
C2	0.0585 (11)	0.0549 (11)	0.0557 (11)	0.0042 (9)	0.0099 (9)	-0.0129 (9)
C3	0.0567 (11)	0.0713 (13)	0.0406 (10)	-0.0023 (9)	0.0063 (8)	-0.0125 (9)
C4	0.0398 (9)	0.0612 (11)	0.0362 (9)	-0.0027 (8)	0.0036 (7)	0.0018 (8)
C5	0.0307 (8)	0.0468 (9)	0.0328 (8)	-0.0008 (6)	0.0049 (6)	0.0055 (7)
C6	0.0639 (12)	0.0747 (13)	0.0333 (9)	-0.0030 (10)	-0.0013 (8)	0.0078 (9)
C7	0.0568 (11)	0.0685 (13)	0.0422 (10)	0.0011 (9)	-0.0019 (8)	0.0214 (9)
C8	0.0355 (9)	0.0518 (10)	0.0430 (9)	-0.0009 (7)	0.0045 (7)	0.0144 (7)
C9	0.0301 (8)	0.0432 (9)	0.0354 (8)	-0.0011 (6)	0.0056 (6)	0.0091 (7)
C10	0.0482 (10)	0.0480 (10)	0.0603 (12)	0.0058 (8)	0.0051 (9)	0.0234 (9)
C11	0.0540 (10)	0.0400 (9)	0.0611 (12)	0.0059 (7)	0.0121 (9)	0.0102 (8)
C12	0.0496 (10)	0.0401 (9)	0.0447 (9)	0.0034 (7)	0.0080 (8)	0.0046 (7)
N1	0.0409 (7)	0.0419 (7)	0.0380 (7)	0.0046 (6)	0.0071 (6)	0.0032 (6)
N2	0.0397 (7)	0.0395 (7)	0.0362 (7)	0.0021 (5)	0.0062 (6)	0.0064 (6)
O1	0.0702 (8)	0.0450 (6)	0.0346 (6)	0.0199 (5)	-0.0025 (5)	0.0063 (5)
O2	0.0850 (9)	0.0415 (6)	0.0373 (6)	0.0096 (6)	0.0093 (6)	0.0062 (5)
O3	0.0905 (9)	0.0455 (7)	0.0360 (6)	0.0270 (6)	0.0032 (6)	0.0077 (5)
O4	0.0538 (7)	0.0472 (7)	0.0644 (8)	0.0162 (5)	0.0151 (6)	0.0198 (6)
O5	0.0678 (8)	0.0517 (7)	0.0620 (8)	0.0202 (6)	0.0188 (6)	0.0226 (6)
O6	0.0742 (9)	0.0463 (7)	0.0606 (8)	0.0099 (6)	0.0266 (7)	0.0060 (6)

Geometric parameters (Å, °)

B1—O2	1.351 (2)	C6—H6A	0.9300
B1—O1	1.355 (2)	C7—C8	1.433 (2)
B1—O3	1.361 (2)	C7—H7	0.9300
B2—O6	1.349 (2)	C8—C10	1.402 (2)

B2—O5	1.359 (2)	C8—C9	1.411 (2)
B2—O4	1.367 (2)	C9—N2	1.3612 (19)
C1—N1	1.323 (2)	C10—C11	1.358 (2)
C1—C2	1.393 (2)	C10—H10	0.9300
C1—H1A	0.9300	C11—C12	1.397 (2)
C2—C3	1.355 (3)	C11—H11	0.9300
C2—H2A	0.9300	C12—N2	1.3207 (19)
C3—C4	1.404 (2)	C12—H12	0.9300
C3—H3A	0.9300	O1—H1	0.8500
C4—C5	1.413 (2)	O2—H2	0.8501
C4—C6	1.425 (2)	O3—H3	0.8500
C5—N1	1.3559 (19)	O4—H4	0.8501
C5—C9	1.450 (2)	O5—H5	0.8501
C6—C7	1.336 (3)	O6—H6	0.8501
O2—B1—O1	123.27 (15)	C6—C7—H7	119.5
O2—B1—O3	116.79 (14)	C8—C7—H7	119.5
O1—B1—O3	119.94 (15)	C10—C8—C9	118.24 (15)
O6—B2—O5	121.00 (16)	C10—C8—C7	121.84 (15)
O6—B2—O4	119.75 (15)	C9—C8—C7	119.92 (16)
O5—B2—O4	119.23 (17)	N2—C9—C8	121.47 (14)
N1—C1—C2	124.43 (17)	N2—C9—C5	119.64 (13)
N1—C1—H1A	117.8	C8—C9—C5	118.88 (14)
C2—C1—H1A	117.8	C11—C10—C8	119.70 (15)
C3—C2—C1	118.03 (16)	C11—C10—H10	120.2
C3—C2—H2A	121.0	C8—C10—H10	120.2
C1—C2—H2A	121.0	C10—C11—C12	118.49 (16)
C2—C3—C4	120.11 (16)	C10—C11—H11	120.8
C2—C3—H3A	119.9	C12—C11—H11	120.8
C4—C3—H3A	119.9	N2—C12—C11	124.05 (15)
C3—C4—C5	118.01 (16)	N2—C12—H12	118.0
C3—C4—C6	121.94 (16)	C11—C12—H12	118.0
C5—C4—C6	120.05 (16)	C1—N1—C5	118.04 (13)
N1—C5—C4	121.35 (14)	C12—N2—C9	118.04 (13)
N1—C5—C9	119.78 (13)	B1—O1—H1	115.9
C4—C5—C9	118.86 (14)	B1—O2—H2	113.4
C7—C6—C4	121.23 (16)	B1—O3—H3	114.0
C7—C6—H6A	119.4	B2—O4—H4	113.0
C4—C6—H6A	119.4	B2—O5—H5	113.6
C6—C7—C8	121.04 (16)	B2—O6—H6	108.1

Hydrogen-bond geometry (Å, °)

<i>D—H...A</i>	<i>D—H</i>	<i>H...A</i>	<i>D...A</i>	<i>D—H...A</i>
O1—H1...N2	0.85	1.90	2.7360 (16)	168.9
O2—H2...N1	0.85	1.88	2.7132 (17)	167.4
O3—H3...O1 ⁱ	0.85	1.86	2.7076 (15)	176.8
O4—H4...O3 ⁱ	0.85	1.89	2.7286 (16)	169.1

O5—H5···O4 ⁱⁱ	0.85	1.89	2.7355 (18)	179.0
O6—H6···O2 ⁱⁱⁱ	0.85	1.95	2.7946 (17)	171.8

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