

tert-Butyl 2-(dihydroxyboryl)pyrrole-1-carboxylate

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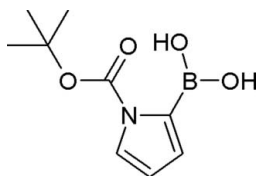
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 Key indicators: single-crystal X-ray study; $T = 100$ K; mean $\sigma(\text{C}-\text{C}) = 0.002$ Å; R factor = 0.031; wR factor = 0.077; data-to-parameter ratio = 14.1.

In the title compound, $\text{C}_9\text{H}_{14}\text{BNO}_4$, the carbonyl and boronic acid groups are essentially coplanar with the pyrrole ring and the boronic acid group has an *exo-endo* conformation. The *exo*-oriented OH is engaged in an intramolecular O—H...O interaction, while the *endo*-oriented one is involved in intermolecular hydrogen bonding to form centrosymmetric dimers. A supramolecular assembly is achieved through interactions involving the *tert*-butyl groups, forming infinite chains along the crystallographic b axis. There are, in addition, face-to-face and center-to-edge stacking interactions [distance between the pyrrole ring centroid and an N atom from a neighbouring molecule = 3.369 (8) Å].

Related literature

For related literature, see: Dabrowski *et al.* (2006); Parry *et al.* (2002); Saygili *et al.* (2004); Seminario *et al.* (1998); Thompson *et al.* (2005); Wang *et al.* (2002).



Experimental

Crystal data

$\text{C}_9\text{H}_{14}\text{BNO}_4$
 $M_r = 211.02$
 Orthorhombic, $Pbca$
 $a = 12.9179$ (12) Å
 $b = 9.5885$ (7) Å
 $c = 17.5811$ (15) Å

$V = 2177.7$ (3) Å³
 $Z = 8$
 Mo $K\alpha$ radiation
 $\mu = 0.10$ mm⁻¹
 $T = 100$ (2) K
 $0.71 \times 0.34 \times 0.22$ mm

Data collection

Kuma KM4 CCD diffractometer
 Absorption correction: multi-scan
 (*CrysAlis RED*; Oxford
 Diffraction 2005)
 $T_{\min} = 0.95$, $T_{\max} = 0.98$

19290 measured reflections
 2713 independent reflections
 1911 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.021$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.031$
 $wR(F^2) = 0.076$
 $S = 0.96$
 2713 reflections

193 parameters
 All H-atom parameters refined
 $\Delta\rho_{\max} = 0.26$ e Å⁻³
 $\Delta\rho_{\min} = -0.19$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$O1-H1O\cdots O3$	0.917 (15)	1.704 (15)	2.5941 (10)	162.9 (13)
$O2-H2O\cdots O1^i$	0.922 (16)	1.855 (17)	2.7728 (11)	173.7 (13)

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

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, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *SHELXL97*.

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

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BG2173).

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supplementary materials

Acta Cryst. (2008). E64, o1054 [doi:10.1107/S1600536808013482]

***tert*-Butyl 2-(dihydroxyboryl)pyrrole-1-carboxylate**

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Comment

Nitrogen-containing boronic acids are the object of interest to many chemists because of their application as potential saccharide sensors (Wang *et al.*, 2002). However, no crystal structure of any boronic acid containing a pyrrole ring has been elucidated to date. The only crystal data concerning nitrogen-containing heterocyclic boronic acids involve some pyridine (Parry *et al.*, 2002), (Thompson *et al.*, 2005), (Dabrowski *et al.*, 2006) and pyrimidine (Saygili *et al.*, 2004) derivatives.

The molecular structure of the title compound $C_9H_{14}BO_4N$ (I) is shown in Fig. 1. The carbonyl and boronic acid groups are essentially coplanar with the pyrrole ring [torsion angles $O3-C5-N1-C1 = -1.31$ (1°) and $N1-C1-B1-O1 = -2.8$ (2°) respectively]. The conformation between C9 from the *tert*-butyl- and the carbonyl groups is antiperiplanar. The boronic acid group has an *exo-endo* conformation. The *exo*-oriented OH is engaged in an intramolecular $O-H\cdots O$ interaction with O3. The *endo*-oriented one, instead, is involved into intermolecular hydrogen bonding to form centrosymmetric dimers (Fig. 2). The supramolecular assembly is achieved through interactions involving *tert*-butyl groups, forming infinite chains along the crystallographic *b* axis. Examination of the crystal packing reveals the presence of face to face, center to edge stacking (FFCE) (Seminario *et al.*, 1998). These interactions are represented by a relatively short distance (3.369 (8) Å) between the pyrrole ring centroid and the nitrogen atom from neighbouring molecules (Fig. 3).

Experimental

N-*tert*-butoxycarbonyl-pyrrole-2-boronic acid was obtained from Aldrich, crystallized from tetrahydrofuran and dried in air.

Refinement

All of hydrogen atoms were located geometrically and their positions were refined while temperature factors were not. The maximum electron-density peak in the final difference map is 0.80 Å from atom C1.

Figures

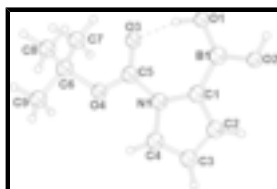


Fig. 1. The molecular structure of (I), showing the atom-labelling scheme. Displacement ellipsoids for all non-H atoms are drawn at the 50% probability level.

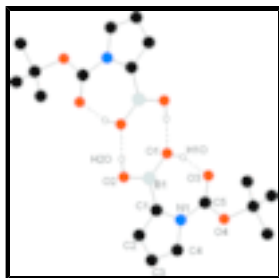


Fig. 2. The hydrogen-bonding pattern for (I). Hydrogen bonds are shown as dashed lines.

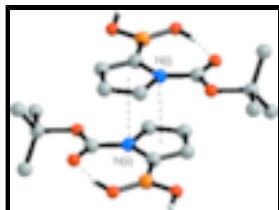


Fig. 3. The crystal packing for (I), showing π - π interactions as dotted lines [Symmetry codes: (i) $-1/2 + x, 1.5 - y, 1 - z$; (ii) $0.5 - x, -1/2 + y, z$].

tert-Butyl 2-(dihydroxyboryl)pyrrole-1-carboxylate

Crystal data

$C_9H_{14}BNO_4$

$M_r = 211.02$

Orthorhombic, *Pbca*

Hall symbol: $-P\ 2ac\ 2ab$

$a = 12.9179\ (12)\ \text{\AA}$

$b = 9.5885\ (7)\ \text{\AA}$

$c = 17.5811\ (15)\ \text{\AA}$

$V = 2177.7\ (3)\ \text{\AA}^3$

$Z = 8$

$F_{000} = 896$

$D_x = 1.287\ \text{Mg m}^{-3}$

Mo $K\alpha$ radiation

$\lambda = 0.71073\ \text{\AA}$

Cell parameters from 19290 reflections

$\theta = 2.8\text{--}28.7^\circ$

$\mu = 0.10\ \text{mm}^{-1}$

$T = 100\ (2)\ \text{K}$

Prismatic, colourless

$0.71 \times 0.34 \times 0.22\ \text{mm}$

Data collection

Kuma KM4 CCD
diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

Detector resolution: $8.6479\ \text{pixels mm}^{-1}$

$T = 100\ (2)\ \text{K}$

ω scan

Absorption correction: multi-scan
(CrysAlis RED; Oxford Diffraction 2005)

$T_{\min} = 0.95, T_{\max} = 0.98$

19290 measured reflections

2713 independent reflections

1911 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.021$

$\theta_{\max} = 28.7^\circ$

$\theta_{\min} = 2.8^\circ$

$h = -17 \rightarrow 17$

$k = -12 \rightarrow 12$

$l = -23 \rightarrow 23$

Refinement

Refinement on F^2

Hydrogen site location: inferred from neighbouring sites

Least-squares matrix: full	All H-atom parameters refined
$R[F^2 > 2\sigma(F^2)] = 0.031$	$w = 1/[\sigma^2(F_o^2) + (0.0461P)^2]$
$wR(F^2) = 0.076$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.97$	$(\Delta/\sigma)_{\max} = 0.001$
2713 reflections	$\Delta\rho_{\max} = 0.26 \text{ e } \text{\AA}^{-3}$
193 parameters	$\Delta\rho_{\min} = -0.19 \text{ e } \text{\AA}^{-3}$
Primary atom site location: structure-invariant direct methods	Extinction correction: SHELXL, $F_c^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Secondary atom site location: difference Fourier map	Extinction coefficient: 0.0033 (7)

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 (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
O1	0.54350 (6)	0.63771 (7)	0.45212 (4)	0.02586 (19)
O2	0.40336 (6)	0.64180 (8)	0.53731 (4)	0.02619 (19)
O3	0.60617 (5)	0.83554 (7)	0.36263 (4)	0.02260 (18)
O4	0.56150 (5)	1.04637 (7)	0.31656 (4)	0.02186 (18)
N1	0.46192 (6)	0.95162 (8)	0.40642 (4)	0.01800 (19)
C1	0.42176 (8)	0.85423 (10)	0.45945 (5)	0.0187 (2)
C2	0.33504 (8)	0.91604 (11)	0.48868 (6)	0.0223 (2)
C3	0.32126 (8)	1.05007 (11)	0.45569 (6)	0.0242 (2)
C4	0.39900 (8)	1.06957 (10)	0.40571 (6)	0.0218 (2)
C5	0.54985 (8)	0.93691 (9)	0.36119 (5)	0.0186 (2)
C6	0.64575 (8)	1.04984 (10)	0.25803 (5)	0.0225 (2)
C7	0.63032 (10)	0.93008 (12)	0.20274 (6)	0.0285 (3)
C8	0.75028 (9)	1.04896 (12)	0.29709 (6)	0.0269 (2)
C9	0.62477 (10)	1.18889 (12)	0.22011 (7)	0.0304 (3)
B1	0.46066 (9)	0.70564 (12)	0.48297 (6)	0.0204 (2)
H1O	0.5763 (11)	0.6964 (15)	0.4187 (8)	0.056 (4)*
H2O	0.4234 (12)	0.5504 (17)	0.5442 (8)	0.060 (5)*
H2	0.2915 (8)	0.8741 (11)	0.5269 (5)	0.018 (2)*
H3	0.2680 (9)	1.1122 (12)	0.4668 (6)	0.028 (3)*
H4	0.4168 (8)	1.1463 (11)	0.3729 (6)	0.020 (3)*
H7A	0.5580 (11)	0.9321 (12)	0.1830 (7)	0.038 (3)*

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H7B	0.6429 (9)	0.8387 (12)	0.2253 (6)	0.029 (3)*
H7C	0.6788 (9)	0.9424 (11)	0.1603 (6)	0.029 (3)*
H8A	0.7576 (9)	1.1342 (13)	0.3317 (7)	0.038 (3)*
H8B	0.7629 (9)	0.9613 (12)	0.3252 (6)	0.031 (3)*
H8C	0.8046 (10)	1.0547 (12)	0.2579 (7)	0.036 (3)*
H9A	0.6288 (8)	1.2649 (12)	0.2567 (7)	0.034 (3)*
H9B	0.5551 (10)	1.1878 (13)	0.1981 (6)	0.040 (3)*
H9C	0.6768 (9)	1.2037 (12)	0.1802 (7)	0.039 (3)*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0238 (4)	0.0218 (4)	0.0320 (4)	0.0014 (3)	0.0056 (3)	0.0085 (3)
O2	0.0255 (4)	0.0253 (4)	0.0278 (4)	-0.0001 (3)	0.0051 (3)	0.0059 (3)
O3	0.0227 (4)	0.0186 (4)	0.0265 (4)	0.0021 (3)	0.0044 (3)	0.0032 (3)
O4	0.0240 (4)	0.0180 (4)	0.0235 (4)	0.0007 (3)	0.0031 (3)	0.0038 (3)
N1	0.0172 (4)	0.0178 (4)	0.0190 (4)	0.0001 (3)	-0.0011 (3)	-0.0005 (3)
C1	0.0181 (5)	0.0220 (5)	0.0159 (4)	-0.0040 (4)	-0.0023 (4)	-0.0013 (4)
C2	0.0188 (5)	0.0286 (6)	0.0194 (5)	-0.0018 (4)	-0.0009 (4)	-0.0039 (4)
C3	0.0195 (5)	0.0264 (6)	0.0267 (5)	0.0049 (5)	-0.0040 (4)	-0.0071 (4)
C4	0.0220 (5)	0.0194 (5)	0.0239 (5)	0.0029 (4)	-0.0061 (4)	-0.0022 (4)
C5	0.0203 (5)	0.0170 (5)	0.0186 (5)	-0.0027 (4)	-0.0026 (4)	-0.0011 (4)
C6	0.0245 (6)	0.0228 (5)	0.0203 (5)	-0.0023 (4)	0.0036 (4)	0.0031 (4)
C7	0.0341 (7)	0.0281 (6)	0.0233 (6)	-0.0037 (5)	0.0027 (5)	-0.0002 (4)
C8	0.0258 (6)	0.0270 (6)	0.0278 (6)	-0.0045 (5)	0.0011 (5)	0.0047 (5)
C9	0.0339 (7)	0.0270 (6)	0.0304 (6)	-0.0027 (5)	0.0012 (5)	0.0087 (5)
B1	0.0193 (6)	0.0230 (6)	0.0190 (5)	-0.0038 (5)	-0.0027 (5)	-0.0013 (5)

Geometric parameters (\AA , $^\circ$)

O1—B1	1.3652 (13)	C3—H3	0.931 (12)
O1—H1O	0.917 (15)	C4—H4	0.963 (10)
O2—B1	1.3547 (13)	C6—C8	1.5149 (15)
O2—H2O	0.922 (16)	C6—C9	1.5151 (14)
O3—C5	1.2143 (11)	C6—C7	1.5176 (14)
O4—C5	1.3191 (11)	C7—H7A	0.996 (13)
O4—C6	1.4981 (12)	C7—H7B	0.976 (11)
N1—C4	1.3928 (12)	C7—H7C	0.981 (12)
N1—C5	1.3937 (12)	C8—H8A	1.023 (13)
N1—C1	1.4178 (12)	C8—H8B	0.989 (12)
C1—C2	1.3676 (14)	C8—H8C	0.985 (13)
C1—B1	1.5665 (15)	C9—H9A	0.973 (12)
C2—C3	1.4211 (15)	C9—H9B	0.980 (13)
C2—H2	0.964 (10)	C9—H9C	0.983 (12)
C3—C4	1.3474 (15)		
B1—O1—H1O	108.9 (9)	O4—C6—C7	109.13 (8)
B1—O2—H2O	111.6 (9)	C8—C6—C7	113.78 (9)
C5—O4—C6	120.61 (7)	C9—C6—C7	111.13 (9)

C4—N1—C5	123.55 (8)	C6—C7—H7A	109.4 (7)
C4—N1—C1	109.10 (8)	C6—C7—H7B	113.4 (6)
C5—N1—C1	127.35 (8)	H7A—C7—H7B	108.4 (10)
C2—C1—N1	105.15 (8)	C6—C7—H7C	108.2 (6)
C2—C1—B1	123.90 (9)	H7A—C7—H7C	109.3 (9)
N1—C1—B1	130.94 (9)	H7B—C7—H7C	108.1 (9)
C1—C2—C3	109.95 (9)	C6—C8—H8A	110.3 (7)
C1—C2—H2	124.0 (6)	C6—C8—H8B	112.2 (7)
C3—C2—H2	126.0 (6)	H8A—C8—H8B	111.5 (9)
C4—C3—C2	107.35 (9)	C6—C8—H8C	108.5 (7)
C4—C3—H3	126.8 (7)	H8A—C8—H8C	107.8 (9)
C2—C3—H3	125.9 (7)	H8B—C8—H8C	106.2 (9)
C3—C4—N1	108.44 (9)	C6—C9—H9A	111.0 (7)
C3—C4—H4	132.4 (6)	C6—C9—H9B	109.2 (7)
N1—C4—H4	119.1 (6)	H9A—C9—H9B	108.6 (10)
O3—C5—O4	125.51 (9)	C6—C9—H9C	108.6 (7)
O3—C5—N1	123.88 (8)	H9A—C9—H9C	109.1 (10)
O4—C5—N1	110.60 (8)	H9B—C9—H9C	110.4 (9)
O4—C6—C8	109.64 (8)	O2—B1—O1	119.54 (10)
O4—C6—C9	101.06 (8)	O2—B1—C1	114.96 (9)
C8—C6—C9	111.34 (9)	O1—B1—C1	125.49 (9)
C4—N1—C1—C2	0.54 (10)	C4—N1—C5—O3	178.49 (9)
C5—N1—C1—C2	-179.63 (8)	C1—N1—C5—O3	-1.32 (14)
C4—N1—C1—B1	179.79 (9)	C4—N1—C5—O4	-2.55 (12)
C5—N1—C1—B1	-0.38 (15)	C1—N1—C5—O4	177.64 (8)
N1—C1—C2—C3	-0.70 (10)	C5—O4—C6—C8	-64.93 (11)
B1—C1—C2—C3	179.99 (9)	C5—O4—C6—C9	177.47 (8)
C1—C2—C3—C4	0.62 (11)	C5—O4—C6—C7	60.31 (11)
C2—C3—C4—N1	-0.26 (11)	C2—C1—B1—O2	-1.97 (14)
C5—N1—C4—C3	179.99 (8)	N1—C1—B1—O2	178.91 (9)
C1—N1—C4—C3	-0.17 (10)	C2—C1—B1—O1	176.28 (10)
C6—O4—C5—O3	3.95 (14)	N1—C1—B1—O1	-2.85 (16)
C6—O4—C5—N1	-174.99 (7)		

Hydrogen-bond geometry (\AA , $^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1—H10 \cdots O3	0.917 (15)	1.704 (15)	2.5941 (10)	162.9 (13)
O2—H20 \cdots O1 ⁱ	0.922 (16)	1.855 (17)	2.7728 (11)	173.7 (13)

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

Fig. 1

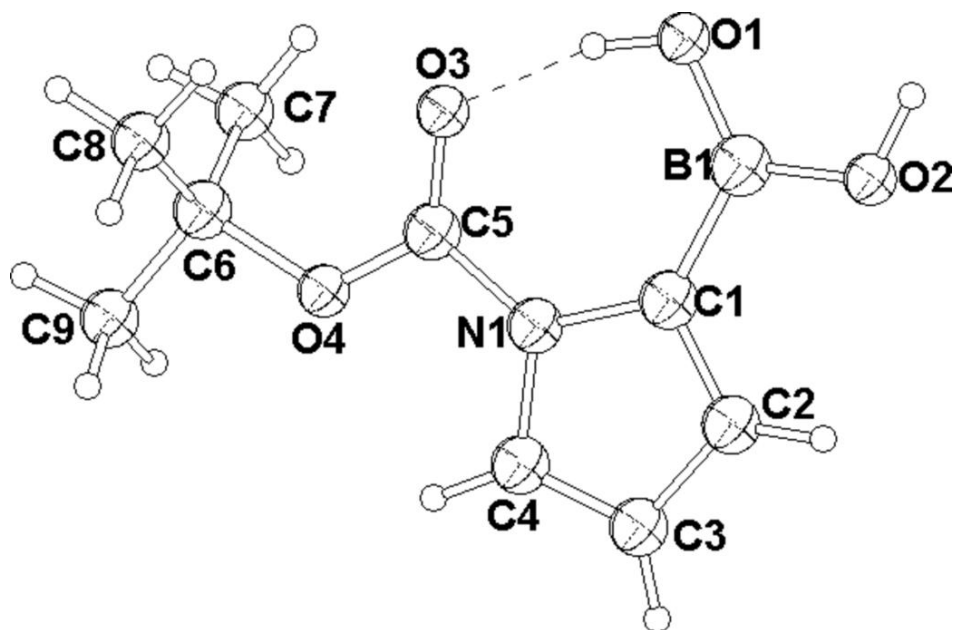


Fig. 2

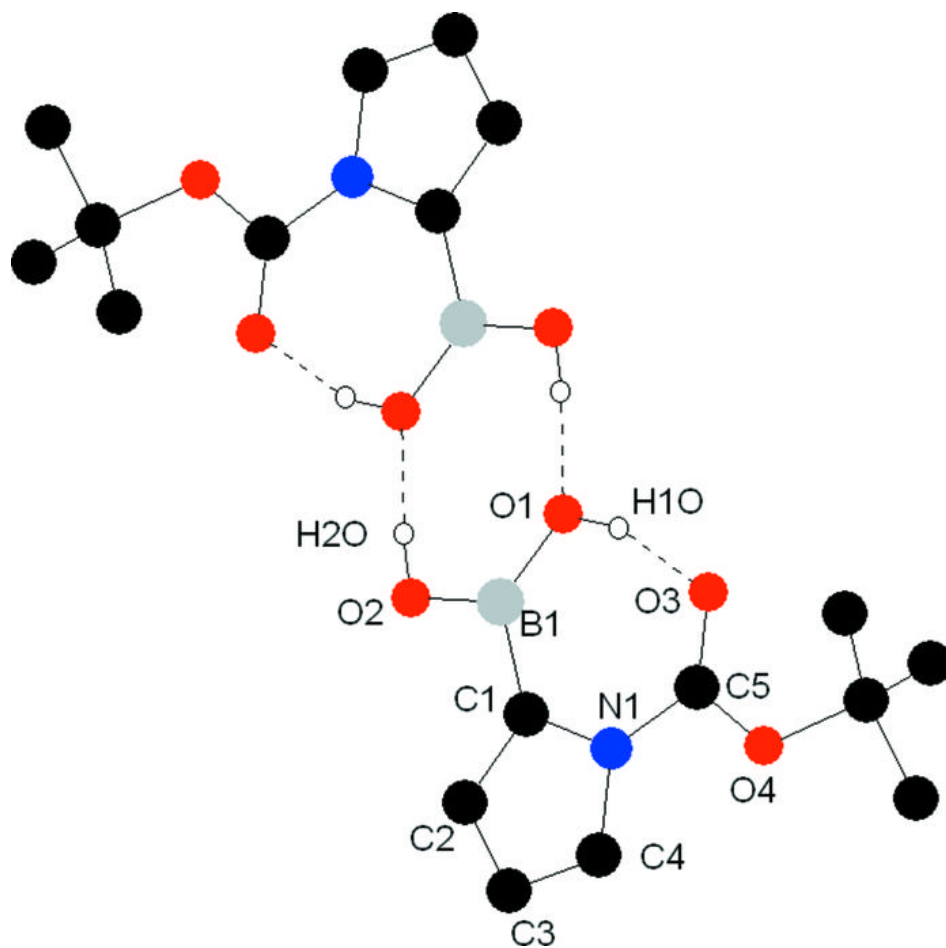


Fig. 3

