

## 2-(6-Bromopyridin-2-yl)-6-methyl-[1,3,6,2]dioxazaborocane, a new stable (pyridin-2-yl)boronic acid derivative

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Received 20 April 2004

Accepted 15 June 2004

Online 21 July 2004

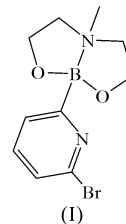
The crystal structure of the first reported non-substituted *N*-methyl-dioxazaborocane confirms that the presence of a methyl group attached to the N atom introduces an N→B bond length that is longer than that in a simple dioxazaborocane ring. The presence of more N atoms in the vicinity of the B atom in the title compound [systematic name: 6a-(6-bromopyridin-2-yl)-3a-methyl-2,3,4,5-tetrahydro-1,6-dioxazaborocane], C<sub>10</sub>H<sub>14</sub>BBrN<sub>2</sub>O<sub>2</sub>, does not modify significantly any structural parameter in the dioxazaborocane ring. On the other hand, a small asymmetry appears in the bond angles of the pyridine C atom next to the B atom.

### Comment

As part of our study of pyridinylboron derivatives, we have recently focused on dioxazaborocanes. These compounds are very interesting since they can undergo internal B←N dative bonding, which leads to a tetracoordinated B atom. Such boron derivatives are expected to be more stable and easier to purify than the corresponding acids or dialkyl esters. To date, only a few crystallographic studies have been carried out on such compounds, and those that have been published do not relate to *N*-methyl-dioxazaborocanes (Iwanek *et al.*, 2002; Höpfl, Sanchez, Barba *et al.*, 1998; Höpfl, Sanchez, Farfan & Barba, 1998).

Crystallographic studies are of particular interest in the field of (pyridin-2-yl)boronic acid derivatives, since the stability of such compounds is not clearly established. On the one hand, different authors have shown the instability of some (pyridin-2-yl)boronic acids and esters (Fischer & Havinga, 1974; Ishiyama *et al.*, 2001). On the other hand, we have prepared, isolated and crystallized some stable (pyridin-2-yl)boron derivatives (Bouillon *et al.*, 2003; Sopková-de Oliveira Santos *et al.*, 2003). The aim of the present study is to understand the effect of a second N atom in the vicinity of the B atom.

According to the literature (Murafaji *et al.*, 1996), the N atom in pyridine can also undergo dative bonding, a fact that is often the cause of instability of (pyridin-2-yl)boron compounds. In the title compound, (I), the pyridine N atom is situated close to the B atom and could influence the dative B←N dioxazaborocane bond.



In the crystal structure of (I) (Fig. 1), the N atom of the dioxazaborocane ring system lies next to the B atom, as expected. The dioxazaborocane moiety comprises two fused five-membered rings, an arrangement that is reported for all structures containing a dioxazaborocane ring system deposited in the Cambridge Structural Database to date (CSD; Version 5.24; Allen, 2002). For the comparison below, structures containing only non-substituted dioxazaborocane ring systems were selected (Rettig & Trotter, 1975; Thadani *et al.*, 2001, 2002; Doidge-Harrison *et al.*, 1998; Caron & Hawkins, 1998; Howie *et al.*, 1997).

Among these structures, two kinds of conformations for the double ring can be observed, *viz.* either 'boat-like' or 'chair-like' conformations. The dioxazaborocane ring in (I) is in a 'chair-like' conformation. In the structure of *B*-phenyl-diptychboroxazolidine, (II) (Rettig & Trotter, 1975), the most closely related compound, the dioxazaborocane ring is also in a 'chair-like' conformation, but oriented differently from that in (I); in (I), the part oriented towards the pyridine ring is that situated on the side of the pyridine ring containing the N atom, contrary to what was observed in (II). The distance between dioxazaborocane atom O2 and pyridine atom N2 [O··N = 2.923 (6) Å] in (I) is similar to the distance between the corresponding O atom and phenyl C atom in (II) (O··C = 2.964 Å).

The introduction of the N atom does not seem to influence either the bond lengths or the bond angles in the vicinity of the B atom. All observed values are close to the means calculated

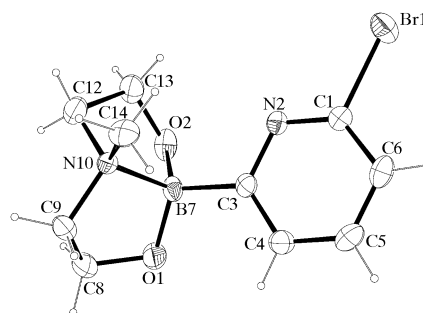
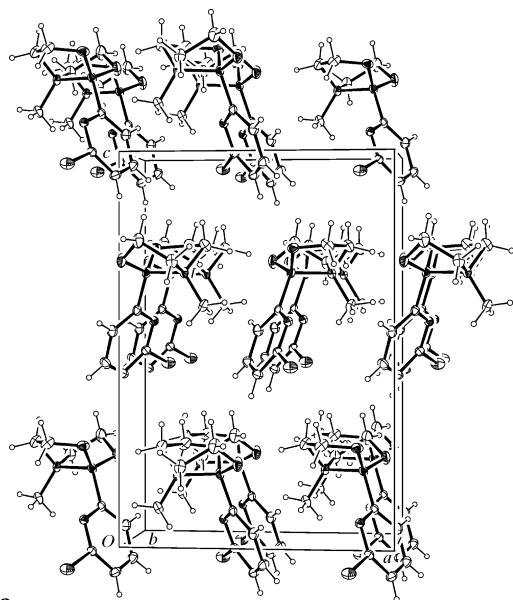


Figure 1

A view of (I), showing the labelling of the non-H atoms. Displacement ellipsoids are shown at the 30% probability level and H atoms are drawn as small circles of arbitrary radii.



**Figure 2**  
A general view of the crystal packing of (I), projected along the *b* axis. Displacement ellipsoids are drawn at the 20% probability level.

from the CSD structures (Table 2). Only one significant difference was observed for (I): the B←N distance is 1.696 (7) Å, significantly longer than the mean value, 1.661 Å, calculated from the data available (Table 2). As the calculated parameter describing the tetrahedral character of boron (THC<sub>DA</sub>; Höpfl, 1999) is the same for both (I) (THC<sub>DA</sub> = 66%) and (II) (THC<sub>DA</sub> = 66%), the reason for the longer B—N bond length might be the presence of a methyl group bound to the dioxazaborocane N atom. To confirm this hypothesis, a second search of the CSD was carried out and structures containing an *N*-methyldioxazaborocane ring were selected (Table 2). These structures do not contain a simple motif; they are either dioxazaborocane-4,8-dione (Mancilla *et al.*, 1997) or dioxazaborocane-4-one (Farfan *et al.*, 1990). The B←N bond length in these structures varies from 1.66 to 1.72 Å, close to the value observed in (I). Furthermore, a dissymmetry in the bond angles around atom C3, the pyridine C atom attached to the B atom, is observed in (I) (Table 1).

The dioxazaborocane cycle is positioned approximately perpendicularly with respect to the pyridine ring, as in all of the CSD structures. The angle between the plane of the pyridine ring and the plane through atoms O1, O2 and N10 is ~87.69 (18)°, similar to that observed in (II) (~89.05°).

In the crystal packing, two layers can be distinguished along the *c* axis, the first containing pyridine rings and the other formed by dioxazaborocane rings. No hydrogen bonds or stacking interactions between pyridine rings were detected in the crystal packing (Fig. 2).

## Experimental

The title compound was synthesized from 2,6-dibromopyridine using the method described by Bouillon *et al.* (2003). Crystals of (I) suitable for X-ray analysis were obtained by slow evaporation from acetonitrile at room temperature.

## Crystal data

C<sub>10</sub>H<sub>14</sub>BBrN<sub>2</sub>O<sub>2</sub>  
*M<sub>r</sub>* = 284.95  
 Orthorhombic, *Pca*2<sub>1</sub>  
*a* = 10.7716 (12) Å  
*b* = 7.0104 (7) Å  
*c* = 15.5546 (14) Å  
*V* = 1174.6 (2) Å<sup>3</sup>  
*Z* = 4  
*D<sub>x</sub>* = 1.611 Mg m<sup>-3</sup>

## Data collection

Enraf-Nonius CAD-4  
 diffractometer  
 θ/2θ scans  
 Absorption correction: Gaussian  
 (JANA2000; Petříček & Dušek,  
 2000)  
*T<sub>min</sub>* = 0.250, *T<sub>max</sub>* = 0.707  
 1767 measured reflections  
 1767 independent reflections

## Refinement

Refinement on *F*<sup>2</sup>  
*R* [*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.049  
*wR* (*F*<sup>2</sup>) = 0.144  
*S* = 1.06  
 1767 reflections  
 146 parameters

Mo *K*α radiation  
 Cell parameters from 25  
 reflections  
 θ = 18–24°  
 μ = 3.49 mm<sup>-1</sup>  
*T* = 293 (2) K  
 Prism, colourless  
 0.65 × 0.63 × 0.29 mm

1408 reflections with *I* > 2σ(*I*)  
 θ<sub>max</sub> = 30.0°  
*h* = 0 → 15  
*k* = 0 → 9  
*l* = -21 → 0  
 3 standard reflections  
 frequency: 60 min  
 intensity decay: 5.5%

H-atom parameters constrained  
*w* = 1/[σ<sup>2</sup>(*F*<sub>o</sub><sup>2</sup>) + (0.1027*P*)<sup>2</sup>]  
 where *P* = (*F*<sub>o</sub><sup>2</sup> + 2*F*<sub>c</sub><sup>2</sup>)/3  
 (Δσ)<sub>max</sub> < 0.001  
 Δρ<sub>max</sub> = 0.74 e Å<sup>-3</sup>  
 Δρ<sub>min</sub> = -0.78 e Å<sup>-3</sup>

**Table 1**

Selected geometric parameters (Å, °).

B7—O1	1.440 (8)	C8—C9	1.514 (10)
B7—O2	1.446 (9)	C13—C12	1.498 (8)
B7—N10	1.696 (7)	C12—N10	1.501 (8)
O1—C8	1.421 (9)	N10—C9	1.496 (6)
O2—C13	1.400 (9)		
N2—C3—C4	119.1 (5)	C4—C3—B7	123.8 (5)
N2—C3—B7	117.1 (5)		

**Table 2**

Comparison of B—N, B—O, B—C and N—C distances (Å) of reported dioxazaborocane rings with those of (I).

B—N10	B—O1	B—O2	B—C3	N10—C14	Reference
1.696 (7)	1.440 (8)	1.446 (9)	1.615 (8)	1.479 (7)	<i>a</i>
1.660	1.469	1.456	1.610		<i>b</i>
1.672	1.471	1.467	1.587		<i>c</i>
1.672	1.459	1.448	1.598		<i>d</i>
1.662	1.478	1.446	1.591		<i>e</i>
1.657	1.459	1.469	1.588		<i>f</i>
1.644	1.457	1.455	1.610		<i>f</i>
1.659	1.466	1.463	1.606		<i>c</i>
1.666	1.462	1.456	1.620		<i>g</i>
1.658	1.464	1.448	1.613		<i>g</i>
1.714	1.422	1.506	1.585	1.472	<i>h</i>
1.719	1.440	1.480	1.592	1.482	<i>h</i>
1.714	1.410	1.529	1.595	1.499	<i>h</i>
1.661	1.460	1.493	1.571	1.493	<i>i</i>
1.672	1.480	1.470	1.561	1.490	<i>i</i>

References: (*a*) this work; (*b*) Rettig & Trotter (1975); (*c*) Thadani *et al.* (2001); (*d*) Doidge-Harrison *et al.* (1998); (*e*) Thadani *et al.* (2002); (*f*) Caron & Hawkins (1998); (*g*) Howie *et al.* (1997); (*h*) Farfan *et al.* (1990); (*i*) Mancilla *et al.* (1997).

H atoms were treated as riding, with C—H distances in the range 0.93–0.96 Å (Sheldrick, 1997). The Flack (1983) value of 0.00 (5) shows that the correct direction of the polar axis has been determined.

Data collection: *CAD-4-PC Software* (Enraf–Nonius, 1996); cell refinement: *CAD-4-PC Software*; data reduction: *JANA2000* (Petříček & Dušek, 2000); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

The authors thank the CRIHAN, the 'Région Haute-Normandie' and the European Community (FEDER).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: DN1051). Services for accessing these data are described at the back of the journal.

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