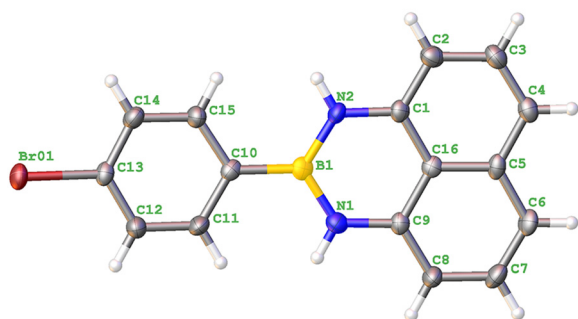


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# The crystal structure of 2-(4-bromophenyl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine, C<sub>16</sub>H<sub>12</sub>BBrN<sub>2</sub>



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## Abstract

C<sub>16</sub>H<sub>12</sub>BBrN<sub>2</sub>, monoclinic, *P*<sub>2</sub><sub>1</sub> (no. 4), *a* = 4.7061(3) Å, *b* = 10.4639(6) Å, *c* = 13.5675(8) Å, β = 97.512(2)°, *V* = 662.39(7) Å<sup>3</sup>, *Z* = 2, *R*<sub>gt</sub>(*F*) = 0.0384, *wR*<sub>ref</sub>(*F*<sup>2</sup>) = 0.0995, *T* = 189.98 K.

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The molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

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Table 1: Data collection and handling.

Crystal:	Colorless needle
Size:	0.10 × 0.08 × 0.06 mm
Wavelength:	Ga Kα radiation (1.34139 Å)
μ:	2.72 mm <sup>-1</sup>
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
θ <sub>max</sub> , completeness:	53.9°, 98%
<i>N</i> ( <i>hkl</i> ) <sub>measured</sub> , <i>N</i> ( <i>hkl</i> ) <sub>unique</sub> , <i>R</i> <sub>int</sub> :	3991, 2427, 0.044
Criterion for <i>I</i> <sub>obs</sub> , <i>N</i> ( <i>hkl</i> ) <sub>gt</sub> :	<i>I</i> <sub>obs</sub> > 2 σ( <i>I</i> <sub>obs</sub> ), 2188
<i>N</i> ( <i>param</i> ) <sub>refined</sub> :	181
Programs:	Bruker [1], Olex2 [2], SHELX [3, 4]

## Source of material

In air, 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (Bpin-B(dan)) (0.1 mmol, 1.0 eq.), 4-bromoaniline (0.2 mmol, 2.0 eq.), TBAI (tetrabutylammonium iodide 0.01 eq.), NaOAc (0.15 eq.), and BPO (0.01 eq.) were sequentially weighed and added to a screw-capped Schlenk tube containing a magnetic stir bar. The vessel was evacuated and refilled with nitrogen. Tert-butyl nitrite (*t*BuONO) (0.2 eq.) and MeCN (0.6 mL) were added in turn under N<sub>2</sub> atmosphere using syringes through a septum which was temporarily used to replace the screw cap. The reaction mixture was then vigorously stirred at 80 °C for the indicated time. The resulting mixture was filtered through a pad of Celite®, and the filter cake was washed with ethyl acetate (3 mL × 2). The combined filtrate was evaporated under vacuum to dryness and the residue was purified by column chromatography to yield the desired product as colorless solid.

## Experimental details

All the H atoms on the benzene rings were placed geometrically and refined without any constraints or restraints.

## Comment

Organoboron compounds, which have been broadly used in synthetic chemistry, drug discovery and materials

**Table 2:** Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å<sup>2</sup>).

Atom	x	Y	z	U <sub>iso</sub> */U <sub>eq</sub>
Br01	1.04997 (8)	0.87888 (9)	0.07431 (3)	0.0290 (2)
N1	0.1275 (7)	0.3841 (8)	0.1996 (3)	0.0263 (8)
H1	0.172177	0.371879	0.139324	0.032*
N2	0.1809 (8)	0.5011 (4)	0.3546 (3)	0.0233 (8)
H2	0.259294	0.563560	0.392208	0.028*
C1	-0.0108 (10)	0.4214 (5)	0.3931 (4)	0.0221 (10)
C2	-0.0826 (11)	0.4377 (6)	0.4887 (4)	0.0279 (11)
H2A	0.001973	0.504833	0.529613	0.033*
C3	-0.2794 (10)	0.3552 (5)	0.5242 (3)	0.0287 (11)
H3	-0.328301	0.367807	0.589212	0.034*
C4	-0.4039 (9)	0.2566 (5)	0.4677 (3)	0.0258 (10)
H4	-0.537117	0.201951	0.493733	0.031*
C5	-0.3332 (9)	0.2358 (5)	0.3697 (4)	0.0230 (9)
C6	-0.4550 (10)	0.1351 (5)	0.3088 (4)	0.0271 (10)
H6	-0.585788	0.077775	0.333244	0.032*
C7	-0.3850 (12)	0.1202 (5)	0.2151 (4)	0.0302 (11)
H7	-0.469792	0.052713	0.174603	0.036*
C8	-0.1906 (10)	0.2023 (5)	0.1773 (4)	0.0264 (10)
H8	-0.143673	0.189401	0.112073	0.032*
C9	-0.0665 (9)	0.3020 (5)	0.2343 (3)	0.0210 (9)
C10	0.4664 (9)	0.5826 (5)	0.2126 (3)	0.0207 (9)
C11	0.5168 (11)	0.5747 (5)	0.1132 (4)	0.0287 (11)
H11	0.427910	0.508311	0.072431	0.034*
C12	0.6916 (11)	0.6605 (6)	0.0728 (4)	0.0287 (11)
H12	0.724365	0.652767	0.005451	0.034*
C13	0.8178 (9)	0.7573 (4)	0.1313 (3)	0.0219 (9)
C14	0.7790 (10)	0.7694 (5)	0.2296 (4)	0.0270 (10)
H14	0.869439	0.836221	0.269481	0.032*
C15	0.6050 (10)	0.6817 (5)	0.2689 (4)	0.0255 (10)
H15	0.578574	0.689028	0.336895	0.031*
C16	-0.1353 (9)	0.3201 (5)	0.3329 (3)	0.0199 (9)
B1	0.2587 (10)	0.4874 (6)	0.2567 (4)	0.0214 (10)

science, have attracted significant attention in recent years [5]. They can react with various functional groups to construct new carbon-carbon bonds or carbon-heteroatom bonds, which can rapidly construct the complex structures of target molecules [6, 7]. When the naphthalene-1,8-diamino (dan) ligand is used as the masking group, which has two nitrogen atoms that may donate their lone pair electrons to the vacant *p*-orbital of the boron atoms, the formed naphthalene-1,8-diamino boronamide (Bdan) compounds are robust enough to avoid undesirable organic reactions, such as Suzuki-Miyaura coupling reaction. Moreover, such compounds can be easily transformed to their corresponding boronic acids by simple treatment under aqueous acidic conditions. These features enable

their wide applications as modular synthetical building blocks [8–10], especially in the iterative cross-coupling reactions and the application of di-boron compounds. So here we report the crystal structure of the title compound (*cf.* figure).

There is one molecule in the symmetric unit (see the figure). All bonds and angles in the crystal structure are within the normal range [11]. In conclusion, we have developed a facile process for the synthesis of 2-(4-bromophenyl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine, C<sub>16</sub>H<sub>12</sub>BBrN<sub>2</sub>.

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