



Crystal structure of the borabenzene–2,6-lutidine adduct

Lauri Kivijärvi and Matti Haukka*

Department of Chemistry, University of Jyväskylä, PO Box 35, FI-40014 Jyväskylä, Finland. *Correspondence e-mail: matti.o.haukka@jyu.fi

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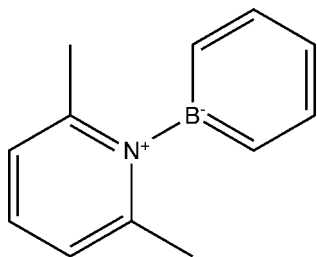
In the title compound, $C_{12}H_{14}BN$, the complete molecule is generated by a crystallographic twofold axis, with two C atoms, the B atom and the N atom lying on the rotation axis. The dihedral angle between the borabenzene and pyridine rings is $81.20(6)^\circ$. As well as dative electron donation from the N atom to the B atom [$B-N = 1.5659(18) \text{ \AA}$], the methyl substituents on the lutidine ring shield the B atom, which further stabilizes the molecule. In the crystal, weak aromatic $\pi-\pi$ stacking between the pyridine rings [centroid–centroid separation = $3.6268(9) \text{ \AA}$] is observed, which generates [001] columns of molecules.

Keywords: crystal structure; borabenzene; $\pi-\pi$ stacking.

CCDC reference: 1434350

1. Related literature

For the synthesis of the title compound, see: Hoic *et al.* (1996). For a related structure, see: Boese *et al.* (1985). For borabenzene adducts as analogues of cyclopentadienyl anions (Cp), see: Bazan *et al.* (2000); Wang *et al.* (2002); Cui *et al.* (2010). For the uses of borabenzene and their metal complexes, see: Wang *et al.* (2002; Jaska *et al.* (2006).



2. Experimental

2.1. Crystal data

$C_{12}H_{14}BN$	$V = 1031.8(4) \text{ \AA}^3$
$M_r = 183.05$	$Z = 4$
Monoclinic, $C2/c$	Mo $K\alpha$ radiation
$a = 10.008(2) \text{ \AA}$	$\mu = 0.07 \text{ mm}^{-1}$
$b = 14.447(3) \text{ \AA}$	$T = 120 \text{ K}$
$c = 7.1360(14) \text{ \AA}$	$0.24 \times 0.18 \times 0.16 \text{ mm}$
$\beta = 90.16(3)^\circ$	

2.2. Data collection

Bruker Kappa APEXII CCD diffractometer	7258 measured reflections
Absorption correction: multi-scan (SADABS; Bruker, 2012)	1482 independent reflections
$T_{\min} = 0.646$, $T_{\max} = 0.746$	1280 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.028$

2.3. Refinement

$R[F^2 > 2\sigma(F^2)] = 0.044$	67 parameters
$wR(F^2) = 0.120$	H-atom parameters constrained
$S = 1.06$	$\Delta\rho_{\text{max}} = 0.30 \text{ e \AA}^{-3}$
1482 reflections	$\Delta\rho_{\text{min}} = -0.17 \text{ e \AA}^{-3}$

Data collection: *COLLECT* (Bruker, 2008); cell refinement: *DENZO/SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO/SCALEPACK*; program(s) used to solve structure: *SUPERFLIP* (Palatinus & Chapuis, 2007); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *CHIMERA* (Pettersen *et al.*, 2004); software used to prepare material for publication: *SHELXL2014*.

Supporting information for this paper is available from the IUCr electronic archives (Reference: HB7526).

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S1. Structural commentary

The title compound lies on a two-fold rotational axis, which passes through atoms H3, C3, B1, N1, C6, and H6.

Borabenzene-2,6-lutidine is an example of nitrogen-stabilized borabenzene adducts. The nitrogen atom of the base (2,5-lutidine) donates an electron pair to the boron atom, and thus stabilizes the borabenzene ring. Borabenzene-2,6-lutidine has a zwitterionic nature. The nitrogen ring bears a positive charge, and the boron ring a negative charge.

Borabenzenes are analogous to cyclopentadienyl anions (Cp), although they are generally weaker electron donors than Cp (Bazan *et al.*, 2000; Wang *et al.*, 2002 and Cui *et al.*, 2010). Borabenzene rings can thus be used as a replacement for Cp when weaker electron donation properties are required. There is a growing interest to utilize borabenzenes and their metal complexes in several applications including catalytic and semiconducting materials as well as light-emitting devices (Wang *et al.*, 2002 and Jaska *et al.*, 2006).

S2. Synthesis and crystallization

The compound was synthesized according to the previously reported procedure (Hoic *et al.* 1996). X-ray quality crystals were obtained by using the following procedure: In a glove box, borabenzene-2,6-lutidine was dissolved in pure toluene at room temperature until a saturated solution was obtained. The clear solution was separated and the solution was allowed to evaporate slowly. Formed crystals were collected from the solution after one week and were immediately taken to an X-ray diffraction analysis. In order to protect the crystals from air and moisture, the crystals were immersed to cryo oil before taking them out from the glove box.

S3. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. Hydrogen atoms were positioned geometrically and constrained to ride on their parent atoms, with C—H = 0.95–0.98 Å and $U_{\text{iso}} = 1.2\text{--}1.5 U_{\text{eq}}(\text{parent atom})$. The highest peak is located 0.69 Å from atom C5 and the deepest hole is located 0.67 Å from atom N1.

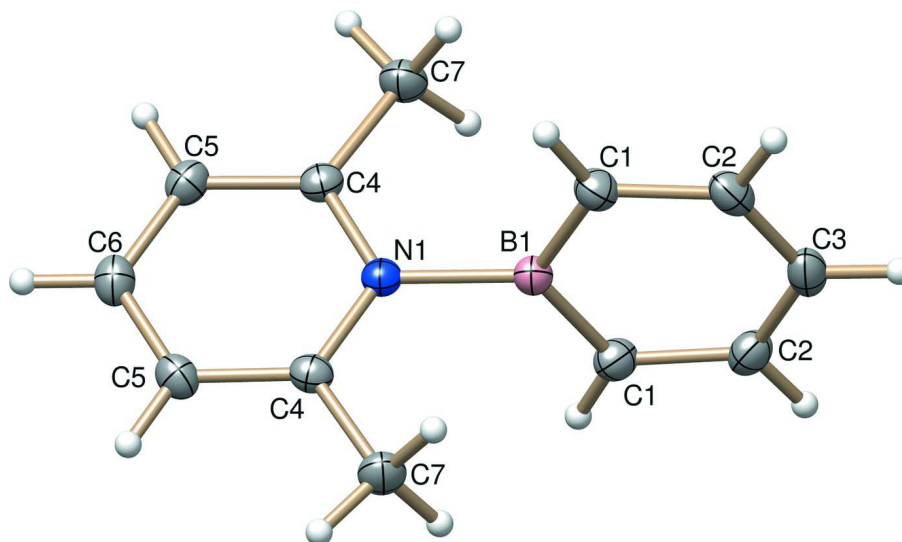


Figure 1

The molecular structure of the title compound, with atom labels and 50% probability displacement ellipsoids for non-H atoms.

Borabenzene-2,6-lutidine

Crystal data

$C_{12}H_{14}BN$

$M_r = 183.05$

Monoclinic, $C2/c$

$a = 10.008(2) \text{ \AA}$

$b = 14.447(3) \text{ \AA}$

$c = 7.1360(14) \text{ \AA}$

$\beta = 90.16(3)^\circ$

$V = 1031.8(4) \text{ \AA}^3$

$Z = 4$

$F(000) = 392$

$D_x = 1.178 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$

Cell parameters from 10098 reflections

$\theta = 1.0\text{--}28.7^\circ$

$\mu = 0.07 \text{ mm}^{-1}$

$T = 120 \text{ K}$

Needle, yellow

$0.24 \times 0.18 \times 0.16 \text{ mm}$

Data collection

Bruker Kappa APEXII CCD
diffractometer

Radiation source: fine-focus sealed tube

Horizontally mounted graphite crystal
monochromator

Detector resolution: $16 \text{ pixels mm}^{-1}$

φ scans and ω scans with κ offset

Absorption correction: multi-scan

(*SADABS*; Bruker, 2012)

$T_{\min} = 0.646$, $T_{\max} = 0.746$

7258 measured reflections

1482 independent reflections

1280 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.028$

$\theta_{\max} = 30.0^\circ$, $\theta_{\min} = 4.0^\circ$

$h = -14 \rightarrow 14$

$k = -16 \rightarrow 20$

$l = -9 \rightarrow 9$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.044$

$wR(F^2) = 0.120$

$S = 1.06$

1482 reflections

67 parameters

0 restraints

Hydrogen site location: inferred from
neighbouring sites

H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0555P)^2 + 0.6142P]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$

$$\Delta\rho_{\max} = 0.30 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.17 \text{ e } \text{\AA}^{-3}$$

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.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
N1	0.5000	0.38254 (7)	0.7500	0.0182 (2)
C1	0.43941 (9)	0.22210 (7)	0.59114 (13)	0.0229 (2)
H1	0.3993	0.2534	0.4883	0.028*
C2	0.44362 (10)	0.12556 (7)	0.59879 (14)	0.0246 (2)
H2	0.4069	0.0910	0.4977	0.030*
C3	0.5000	0.07806 (9)	0.7500	0.0254 (3)
H3	0.5000	0.0123	0.7500	0.031*
C4	0.38816 (9)	0.42921 (7)	0.80474 (12)	0.0197 (2)
C5	0.38693 (9)	0.52523 (7)	0.80370 (13)	0.0225 (2)
H5	0.3086	0.5578	0.8398	0.027*
C6	0.5000	0.57352 (9)	0.7500	0.0241 (3)
H6	0.5000	0.6393	0.7500	0.029*
C7	0.26941 (10)	0.37460 (7)	0.86747 (15)	0.0258 (2)
H7A	0.2957	0.3332	0.9699	0.039*
H7B	0.2351	0.3379	0.7624	0.039*
H7C	0.1996	0.4169	0.9112	0.039*
B1	0.5000	0.27415 (10)	0.7500	0.0195 (3)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0180 (5)	0.0187 (5)	0.0179 (5)	0.000	-0.0021 (4)	0.000
C1	0.0222 (4)	0.0228 (5)	0.0239 (5)	-0.0022 (3)	-0.0018 (3)	0.0003 (3)
C2	0.0222 (4)	0.0235 (5)	0.0282 (5)	-0.0047 (3)	0.0024 (4)	-0.0045 (4)
C3	0.0230 (6)	0.0179 (6)	0.0355 (7)	0.000	0.0068 (5)	0.000
C4	0.0183 (4)	0.0224 (4)	0.0183 (4)	0.0011 (3)	-0.0013 (3)	0.0003 (3)
C5	0.0237 (5)	0.0221 (5)	0.0218 (5)	0.0042 (3)	0.0006 (3)	-0.0004 (3)
C6	0.0309 (7)	0.0193 (6)	0.0220 (6)	0.000	-0.0004 (5)	0.000
C7	0.0195 (4)	0.0268 (5)	0.0312 (5)	-0.0010 (3)	0.0025 (4)	-0.0003 (4)
B1	0.0177 (6)	0.0177 (6)	0.0230 (6)	0.000	-0.0002 (5)	0.000

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

N1—C4 ⁱ	1.3647 (11)	C4—C5	1.3874 (13)
N1—C4	1.3647 (11)	C4—C7	1.4961 (13)
N1—B1	1.5659 (18)	C5—C6	1.3843 (12)

C1—C2	1.3964 (14)	C5—H5	0.9500
C1—B1	1.4881 (12)	C6—C5 ⁱ	1.3843 (12)
C1—H1	0.9500	C6—H6	0.9500
C2—C3	1.3965 (13)	C7—H7A	0.9800
C2—H2	0.9500	C7—H7B	0.9800
C3—C2 ⁱ	1.3966 (13)	C7—H7C	0.9800
C3—H3	0.9500	B1—C1 ⁱ	1.4881 (12)
C4 ⁱ —N1—C4	120.78 (11)	C6—C5—C4	119.88 (9)
C4 ⁱ —N1—B1	119.61 (6)	C6—C5—H5	120.1
C4—N1—B1	119.61 (6)	C4—C5—H5	120.1
C2—C1—B1	117.56 (9)	C5 ⁱ —C6—C5	119.48 (13)
C2—C1—H1	121.2	C5 ⁱ —C6—H6	120.3
B1—C1—H1	121.2	C5—C6—H6	120.3
C1—C2—C3	122.22 (9)	C4—C7—H7A	109.5
C1—C2—H2	118.9	C4—C7—H7B	109.5
C3—C2—H2	118.9	H7A—C7—H7B	109.5
C2—C3—C2 ⁱ	121.13 (13)	C4—C7—H7C	109.5
C2—C3—H3	119.4	H7A—C7—H7C	109.5
C2 ⁱ —C3—H3	119.4	H7B—C7—H7C	109.5
N1—C4—C5	119.99 (9)	C1—B1—C1 ⁱ	119.30 (12)
N1—C4—C7	118.55 (9)	C1—B1—N1	120.35 (6)
C5—C4—C7	121.46 (8)	C1 ⁱ —B1—N1	120.35 (6)
B1—C1—C2—C3	1.10 (12)	C4—C5—C6—C5 ⁱ	0.52 (6)
C1—C2—C3—C2 ⁱ	-0.59 (7)	C2—C1—B1—C1 ⁱ	-0.53 (6)
C4 ⁱ —N1—C4—C5	0.52 (6)	C2—C1—B1—N1	179.47 (6)
B1—N1—C4—C5	-179.47 (6)	C4 ⁱ —N1—B1—C1	-98.80 (6)
C4 ⁱ —N1—C4—C7	-178.65 (9)	C4—N1—B1—C1	81.20 (6)
B1—N1—C4—C7	1.35 (9)	C4 ⁱ —N1—B1—C1 ⁱ	81.20 (6)
N1—C4—C5—C6	-1.05 (12)	C4—N1—B1—C1 ⁱ	-98.80 (6)
C7—C4—C5—C6	178.10 (7)		

Symmetry code: (i) $-x+1, y, -z+3/2$.