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2-(Pyridin-4-yl)-2,3-dihydro-1*H*-naphtho[1,8-*de*]-[1,3,2]diazaborinine

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4-PyBdan

Keywords: crystal structure; pyridine derivative; tetrameric structure; dan.

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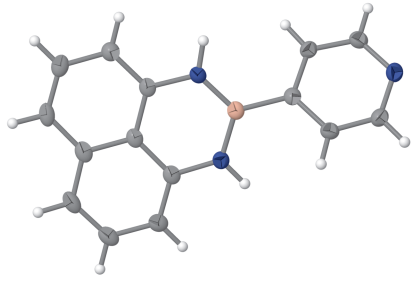
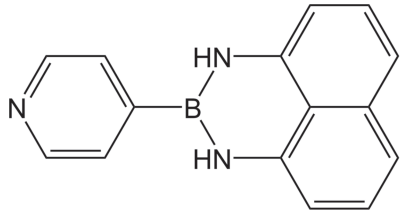
Structural data: full structural data are available from iucrdata.iucr.org

The title compound, $C_{15}H_{12}BN_3$, is a type of diazaborinane featuring substitution at 1, 2, and 3 positions in the nitrogen–boron six-membered heterocycle. It is comprised of two almost planar units, the pyridyl ring and the Bdan (dan = 1,8-diaminonaphtho) group, which subtend a dihedral angle of 24.57 (5)°. In the crystal, the molecules are linked into $R_4^4(28)$ hydrogen-bonding networks around the fourfold inversion axis, giving cyclic tetramers. The molecules form columnar stacks along the *c* axis.

3D view



Chemical scheme



Structure description

The title compound, $C_{15}H_{12}BN_3$, is a type of diazaborinane that is substituted at the 1, 2, and 3 positions in the nitrogen–boron six-membered heterocycle. Recently, diazaborinanes have been found to stabilize organic radicals (LaPorte *et al.*, 2023).

The title molecule (Fig. 1) is comprised of two almost planar units, the N1/C1–C5 pyridyl ring and the N2/N3/C6–C15/B1 group, which subtend a dihedral angle of 24.57 (5)°. This is slightly larger than those in related compounds that have almost planar structures (Akerman *et al.*, 2011; Slabber *et al.*, 2011).

In the crystal, the molecules make $R_4^4(28)$ hydrogen-bonding (Table 1) networks around the fourfold inversion axis, giving a cyclic tetramer as shown in Fig. 2. The formation of this tetrameric structure is thought to increase the dihedral angle. The molecules also stack along the *c* axis, as shown in Fig. 3, forming columnar stacks in which the B1···C6^{ii}, B1···C7^{ii}, and B1···C8^{ii} distances are 3.656 (3), 3.513 (3) and 3.573 (3) Å, respectively [symmetry code:(ii) x, y, $z-1$].

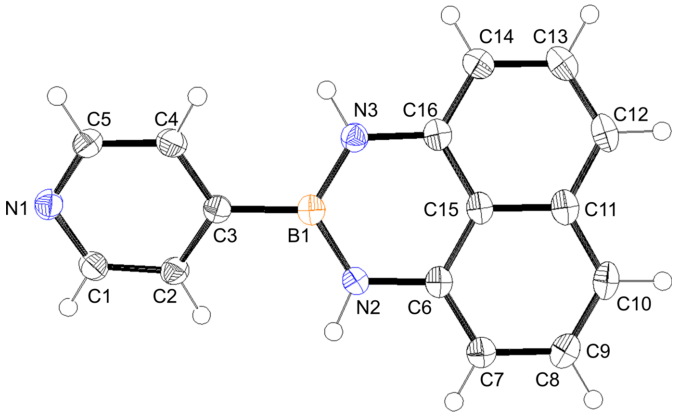


Figure 1
The title compound with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

Synthesis and crystallization

The title compound was prepared according to the literature method (Hashimoto & Okuno, 2024). Single crystals of sufficient quality were obtained by recrystallization from chloroform solution.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

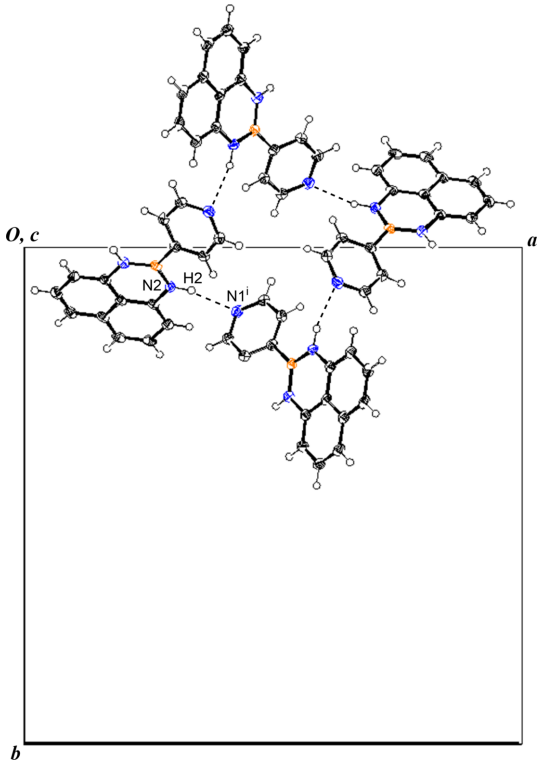


Figure 2
The hydrogen-bonding network of the title compound. [Symmetry code: (i) $y+\frac{1}{2}, -x+\frac{1}{2}, -z-\frac{1}{2}$.]

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2···N1^{i}	0.93 (2)	2.21 (2)	3.113 (2)	162 (2)

Symmetry code: (i) $y+\frac{1}{2}, -x+\frac{1}{2}, -z-\frac{1}{2}$.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{15}H_{12}BN_3$
M_r	245.09
Crystal system, space group	Tetragonal, $I\overline{4}$
Temperature (K)	100
a, c (Å)	21.5659 (3), 5.0863 (1)
V (Å^3)	2365.58 (8)
Z	8
Radiation type	Cu $K\alpha$
μ (mm^{-1})	0.65
Crystal size (mm)	0.20 × 0.05 × 0.05
Data collection	
Diffractometer	XtaLAB Synergy R, DW system, HyPix
Absorption correction	Multi-scan (*CrysAlis PRO*; Rigaku OD, 2024)
T_{min}, T_{max}	0.807, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	7772, 2268, 2125
R_{int}	0.036
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.626
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.031, 0.083, 1.06
No. of reflections	2268
No. of parameters	180
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.15, −0.16
Absolute structure	Flack x determined using 840 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons *et al.*, 2013)
Absolute structure parameter	−0.2 (3)

Computer programs: *CrysAlis PRO* (Rigaku OD, 2024), *SHELXS* (Sheldrick, 2008), *SHELXL2013/2* (Sheldrick, 2015) and *OLEX2* (Dolomanov *et al.*, 2009).

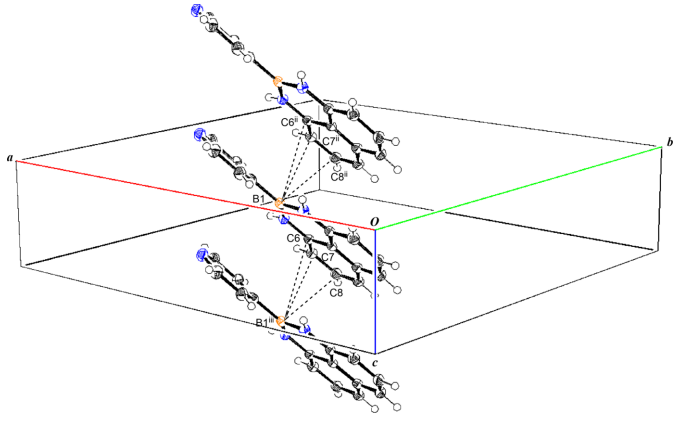


Figure 3
The stacking structure along the c axis. [Symmetry codes:(ii) $x, y, z-1$; (iii) $x, y, z+1$.]

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full crystallographic data

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2-(Pyridin-4-yl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine

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\ 2-(Pyridin-4-yl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]\ diazaborinine

Crystal data

$C_{15}H_{12}BN_3$
M_r = 245.09
Tetragonal, $I\overline{4}$
a = 21.5659 (3) Å
c = 5.0863 (1) Å
V = 2365.58 (8) Å^3
Z = 8
F(000) = 1024
D_x = 1.376 Mg m^{-3}
Cu $K\alpha$ radiation, λ = 1.54184 Å
Cell parameters from 5132 reflections
θ = 2.9–75.0°
μ = 0.65 mm^{-1}
T = 100 K
Block, clear colourless
0.2 × 0.05 × 0.05 mm

Data collection

XtaLAB Synergy R, DW system, HyPix diffractometer
Radiation source: Rotating-anode X-ray tube, Rigaku (Cu) X-ray Source
Mirror monochromator
Detector resolution: 10.0000 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (CrysAlisPro; Rigaku OD, 2024)
T_{min} = 0.807, T_{max} = 1.000
7772 measured reflections
2268 independent reflections
2125 reflections with $I > 2\sigma(I)$
R_{int} = 0.036
θ_{max} = 75.0°, θ_{min} = 2.9°
h = −25→26
k = −26→27
l = −5→6

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.031
$wR(F^2)$ = 0.083
S = 1.06
2268 reflections
180 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0502P)^2 + 0.1789P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.15 e Å^{-3}
$\Delta\rho_{min}$ = −0.15 e Å^{-3}
Absolute structure: Flack x determined using 840 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons *et al.*, 2013)
Absolute structure parameter: −0.2 (3)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. The positions of the N-bound H atoms were obtained from difference Fourier maps and were refined isotropically. The C-bound H atoms were placed at ideal positions and were refined as riding on their parent C atoms. U_{iso}(H) values of the H atoms were set at 1.2U_{eq}(parent atom for Csp^2).

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
N3	0.20041 (7)	0.03150 (8)	−0.0041 (4)	0.0233 (4)
C7	0.28868 (9)	0.15497 (9)	0.5132 (4)	0.0252 (4)
H7	0.3324	0.1604	0.5071	0.030*
C1	0.39265 (9)	−0.01777 (9)	−0.5063 (4)	0.0270 (4)
H1	0.4315	−0.0032	−0.5689	0.032*
N2	0.29394 (8)	0.07934 (7)	0.1587 (3)	0.0217 (3)
C13	0.10022 (9)	0.05895 (9)	0.1820 (4)	0.0267 (4)
H13	0.0797	0.0324	0.0611	0.032*
C10	0.15895 (9)	0.14042 (9)	0.5376 (4)	0.0255 (4)
C15	0.19455 (9)	0.10642 (8)	0.3491 (4)	0.0219 (4)
C5	0.31573 (9)	−0.08947 (9)	−0.5129 (4)	0.0273 (4)
H5	0.2989	−0.1270	−0.5796	0.033*
C6	0.26012 (9)	0.11421 (8)	0.3414 (4)	0.0218 (4)
C14	0.16387 (9)	0.06513 (9)	0.1728 (4)	0.0231 (4)
C11	0.09363 (10)	0.13134 (9)	0.5452 (4)	0.0288 (5)
H11	0.0693	0.1527	0.6721	0.035*
B1	0.26579 (10)	0.03753 (10)	−0.0181 (4)	0.0220 (4)
C3	0.30411 (9)	−0.00146 (9)	−0.2242 (4)	0.0220 (4)
C4	0.28147 (9)	−0.05701 (9)	−0.3271 (4)	0.0262 (4)
H4	0.2426	−0.0727	−0.2700	0.031*
C12	0.06564 (9)	0.09191 (9)	0.3700 (4)	0.0286 (5)
H12	0.0219	0.0868	0.3758	0.034*
N1	0.37087 (8)	−0.07118 (8)	−0.6036 (3)	0.0268 (4)
C2	0.36184 (9)	0.01756 (9)	−0.3191 (4)	0.0246 (4)
H2A	0.3801	0.0547	−0.2555	0.030*
C9	0.19006 (10)	0.18127 (9)	0.7109 (4)	0.0277 (5)
H9	0.1670	0.2039	0.8380	0.033*
C8	0.25310 (10)	0.18841 (9)	0.6969 (4)	0.0279 (4)
H8	0.2732	0.2164	0.8132	0.033*
H3	0.1804 (12)	0.0058 (12)	−0.125 (6)	0.042 (7)*
H2	0.3364 (11)	0.0870 (10)	0.167 (5)	0.028 (6)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N3	0.0236 (8)	0.0238 (8)	0.0225 (8)	0.0017 (6)	−0.0004 (7)	−0.0003 (7)
C7	0.0272 (9)	0.0252 (9)	0.0233 (10)	0.0016 (8)	−0.0001 (8)	0.0025 (8)
C1	0.0229 (9)	0.0263 (9)	0.0317 (10)	0.0004 (8)	0.0016 (9)	0.0004 (9)
N2	0.0203 (8)	0.0225 (7)	0.0223 (8)	0.0012 (6)	0.0012 (7)	0.0008 (7)
C13	0.0254 (10)	0.0260 (9)	0.0287 (10)	−0.0001 (8)	0.0002 (9)	0.0042 (9)
C10	0.0313 (10)	0.0235 (9)	0.0216 (10)	0.0058 (8)	0.0042 (8)	0.0068 (8)

C15	0.0262 (9)	0.0202 (8)	0.0193 (9)	0.0045 (7)	0.0022 (8)	0.0053 (7)
C5	0.0272 (10)	0.0245 (9)	0.0301 (10)	−0.0008 (8)	−0.0020 (9)	−0.0043 (8)
C6	0.0270 (9)	0.0200 (8)	0.0183 (9)	0.0027 (7)	0.0016 (8)	0.0050 (8)
C14	0.0271 (9)	0.0209 (9)	0.0214 (9)	0.0025 (7)	0.0018 (8)	0.0057 (8)
C11	0.0301 (10)	0.0283 (10)	0.0278 (11)	0.0088 (8)	0.0094 (9)	0.0068 (8)
B1	0.0254 (10)	0.0194 (9)	0.0212 (10)	0.0027 (8)	0.0001 (9)	0.0041 (9)
C3	0.0227 (9)	0.0228 (9)	0.0204 (9)	0.0030 (7)	−0.0033 (7)	0.0017 (7)
C4	0.0223 (9)	0.0274 (9)	0.0290 (10)	−0.0008 (8)	−0.0003 (8)	0.0000 (9)
C12	0.0248 (9)	0.0290 (10)	0.0319 (11)	0.0044 (8)	0.0051 (9)	0.0092 (9)
N1	0.0272 (9)	0.0263 (8)	0.0270 (9)	0.0038 (7)	−0.0015 (7)	−0.0034 (7)
C2	0.0253 (9)	0.0210 (9)	0.0276 (10)	−0.0009 (8)	−0.0009 (8)	−0.0012 (8)
C9	0.0383 (11)	0.0243 (10)	0.0205 (10)	0.0092 (8)	0.0042 (9)	0.0014 (8)
C8	0.0387 (11)	0.0223 (9)	0.0226 (10)	0.0035 (8)	−0.0019 (9)	0.0010 (8)

Geometric parameters (Å, º)

N3—C14	1.399 (3)	C10—C9	1.416 (3)
N3—B1	1.418 (3)	C15—C6	1.425 (3)
N3—H3	0.93 (3)	C15—C14	1.426 (3)
C7—H7	0.9500	C5—H5	0.9500
C7—C6	1.384 (3)	C5—C4	1.389 (3)
C7—C8	1.408 (3)	C5—N1	1.335 (3)
C1—H1	0.9500	C11—H11	0.9500
C1—N1	1.339 (3)	C11—C12	1.372 (3)
C1—C2	1.389 (3)	B1—C3	1.578 (3)
N2—C6	1.401 (2)	C3—C4	1.396 (3)
N2—B1	1.411 (3)	C3—C2	1.397 (3)
N2—H2	0.93 (2)	C4—H4	0.9500
C13—H13	0.9500	C12—H12	0.9500
C13—C14	1.380 (3)	C2—H2A	0.9500
C13—C12	1.405 (3)	C9—H9	0.9500
C10—C15	1.431 (3)	C9—C8	1.370 (3)
C10—C11	1.423 (3)	C8—H8	0.9500
C14—N3—B1	123.02 (17)	C13—C14—N3	122.15 (18)
C14—N3—H3	118.1 (17)	C13—C14—C15	120.03 (18)
B1—N3—H3	118.8 (17)	C10—C11—H11	119.9
C6—C7—H7	119.9	C12—C11—C10	120.23 (18)
C6—C7—C8	120.13 (18)	C12—C11—H11	119.9
C8—C7—H7	119.9	N3—B1—C3	120.36 (18)
N1—C1—H1	118.0	N2—B1—N3	117.04 (18)
N1—C1—C2	123.90 (18)	N2—B1—C3	122.60 (17)
C2—C1—H1	118.0	C4—C3—B1	121.57 (17)
C6—N2—B1	122.82 (16)	C4—C3—C2	115.74 (18)
C6—N2—H2	112.8 (15)	C2—C3—B1	122.68 (17)
B1—N2—H2	124.4 (15)	C5—C4—C3	120.12 (18)
C14—C13—H13	119.9	C5—C4—H4	119.9
C14—C13—C12	120.1 (2)	C3—C4—H4	119.9

C12—C13—H13	119.9	C13—C12—H12	119.3
C11—C10—C15	118.62 (19)	C11—C12—C13	121.46 (18)
C9—C10—C15	118.83 (18)	C11—C12—H12	119.3
C9—C10—C11	122.54 (18)	C5—N1—C1	116.03 (17)
C6—C15—C10	119.37 (18)	C1—C2—C3	120.15 (17)
C6—C15—C14	121.14 (17)	C1—C2—H2A	119.9
C14—C15—C10	119.49 (17)	C3—C2—H2A	119.9
C4—C5—H5	118.0	C10—C9—H9	119.7
N1—C5—H5	118.0	C8—C9—C10	120.51 (19)
N1—C5—C4	124.06 (18)	C8—C9—H9	119.7
C7—C6—N2	121.89 (17)	C7—C8—H8	119.4
C7—C6—C15	119.97 (17)	C9—C8—C7	121.19 (19)
N2—C6—C15	118.14 (16)	C9—C8—H8	119.4
N3—C14—C15	117.81 (16)		

N3—B1—C3—C4	−23.9 (3)	C11—C10—C15—C6	−179.01 (17)
N3—B1—C3—C2	154.92 (19)	C11—C10—C15—C14	0.7 (3)
N2—B1—C3—C4	156.09 (19)	C11—C10—C9—C8	179.81 (19)
N2—B1—C3—C2	−25.1 (3)	B1—N3—C14—C13	179.50 (19)
C10—C15—C6—C7	−0.8 (3)	B1—N3—C14—C15	−1.1 (3)
C10—C15—C6—N2	178.65 (16)	B1—N2—C6—C7	179.99 (18)
C10—C15—C14—N3	−178.38 (17)	B1—N2—C6—C15	0.5 (3)
C10—C15—C14—C13	1.0 (3)	B1—C3—C4—C5	178.49 (18)
C10—C11—C12—C13	0.9 (3)	B1—C3—C2—C1	−178.13 (18)
C10—C9—C8—C7	−0.8 (3)	C4—C5—N1—C1	−0.6 (3)
C15—C10—C11—C12	−1.7 (3)	C4—C3—C2—C1	0.7 (3)
C15—C10—C9—C8	0.5 (3)	C12—C13—C14—N3	177.53 (17)
C6—C7—C8—C9	0.3 (3)	C12—C13—C14—C15	−1.8 (3)
C6—N2—B1—N3	−0.3 (3)	N1—C1—C2—C3	−1.1 (3)
C6—N2—B1—C3	179.77 (16)	N1—C5—C4—C3	0.3 (3)
C6—C15—C14—N3	1.4 (3)	C2—C1—N1—C5	0.9 (3)
C6—C15—C14—C13	−179.24 (18)	C2—C3—C4—C5	−0.4 (3)
C14—N3—B1—N2	0.6 (3)	C9—C10—C15—C6	0.3 (3)
C14—N3—B1—C3	−179.47 (17)	C9—C10—C15—C14	−179.93 (16)
C14—C13—C12—C11	0.9 (3)	C9—C10—C11—C12	179.00 (18)
C14—C15—C6—C7	179.45 (17)	C8—C7—C6—N2	−178.96 (17)
C14—C15—C6—N2	−1.1 (3)	C8—C7—C6—C15	0.5 (3)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2···N1^{i}	0.93 (2)	2.21 (2)	3.113 (2)	162 (2)

Symmetry code: (i) *y*+1/2, −*x*+1/2, −*z*−1/2.