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Crystal structure of 2,6-bis[(1*H*-pyrazol-1-yl)methyl]pyridine

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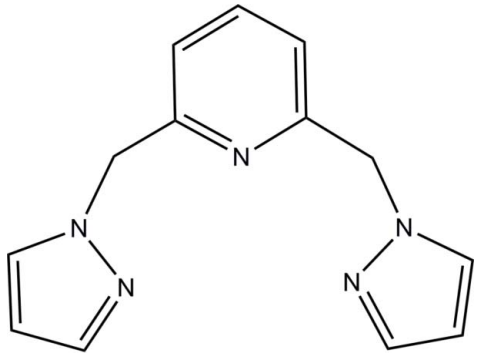
In the title compound, $C_{13}H_{13}N_5$, the planes of the pyrazolyl groups are nearly perpendicular to that of the central pyridine ring, making dihedral angles of 87.77 (8) and 85.73 (7)°. In the crystal, weak C—H···N hydrogen bonds link the molecules into layers extending parallel to $(10\bar{1})$.

Keywords: crystal structure; pyridine; purazole; tridentate ligand; catalysis.

CCDC reference: 1016859

1. Related literature

For the synthesis of the title compound, see: Reger *et al.* (2005). For metal complexes with similar ligands, see: Sharma *et al.* (2011); Ojwach *et al.* (2007); Manikandan *et al.* (2000, 2001); Halcrow & Kilner (2002). For potential applications of the ligand in catalysis, see: Karam *et al.* (2005).



2. Experimental

2.1. Crystal data

$C_{13}H_{13}N_5$
M_r = 239.28
Monoclinic, $P2_1/n$
a = 7.481 (3) Å
b = 9.076 (4) Å
c = 19.021 (8) Å
β = 95.471 (5)°
V = 1285.7 (9) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.08 mm^{-1}
T = 296 K
0.26 × 0.2 × 0.15 mm

2.2. Data collection

Bruker SMART CCD area-detector diffractometer
25319 measured reflections
3136 independent reflections
2260 reflections with $I > 2\sigma(I)$
R_{int} = 0.040

2.3. Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.060
$wR(F^2)$ = 0.149
S = 1.09
3136 reflections
163 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.24 e Å^{-3}
$\Delta\rho_{min}$ = −0.28 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
C4—H4···N15^{i}	0.93	2.62	3.550 (3)	178
C6—H6B···N12^{ii}	0.97	2.54	3.430 (2)	152

Symmetry codes: (i) $x-\frac{1}{2}, -y+\frac{3}{2}, z-\frac{1}{2}$; (ii) $-x+1, -y+2, -z$.

Data collection: *SMART* (Bruker, 2002); cell refinement: *SAINT* (Bruker, 2002); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS2013* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2013* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012); software used to prepare material for publication: *WinGX* (Farrugia, 2012).

Acknowledgements

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Supporting information for this paper is available from the IUCr electronic archives (Reference: IS5371).

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Crystal structure of 2,6-bis[(1*H*-pyrazol-1-yl)methyl]pyridine

Kyung-sun Son, Jeong Oh Woo, Daeyoung Kim and Sung Kwon Kang

S1. Experimental

To a stirred solution of 2,6-pyridinedimethanol (0.28 g, 2 mmol) and NaOH (0.8 g, 20 mmol) in THF/water (7.5/7.5 ml) was added a solution of *p*-toluenesulfonyl chloride (0.761 g, 4 mmol) in THF (7.5 ml) at 0 °C. After 4 h of stirring, the mixture was poured into 20 ml of water and extracted with methylene chloride. The organic phase was washed with saturated aqueous NaCl solution and distilled water and dried over Na_2SO_4, and the solvent was removed *in vacuo* to afford 2,6-pyridine-dimethylene-ditosylate (0.788 g, 88%) as a white powder. In a separate flask under a nitrogen atmosphere, a solution of pyrazole (0.22 g, 3.2 mmol) in dry THF (5 ml) was added dropwise to a suspension of NaH (0.08 g, 3.2 mmol) in dry THF (5 ml) at 0 °C. After 15 min of stirring, a clear solution of NaPz was obtained. A solution of 2,6-pyridine-dimethylene-ditosylate (0.73 g, 1.6 mmol) in dry THF (7.5 ml) was added to this solution; the mixture was stirred overnight and filtered, and the solvent was removed. The crude product was purified by column chromatography on silica gel with ethyl acetate as eluent to afford 0.30 g (76%) of pure ligand as a white solid. Single crystals of the title compound were obtained by slow diffusion of hexane into a concentrated solution of the white solid in THF at room temperature within 1–2 days.

S2. Refinement

All H atoms were positioned geometrically and refined using a riding model, with C—H = 0.93–0.97 Å, and with U_{iso}(H) = 1.2U_{eq}(C).

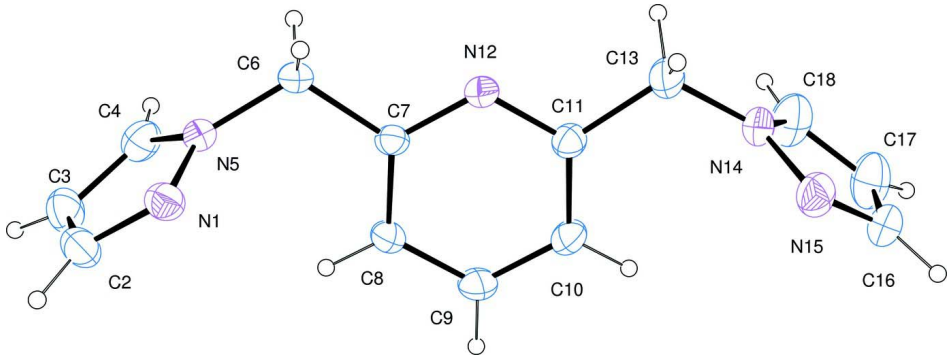

Figure 1

Molecular structure of the title compound, showing the atom-numbering scheme and 30% probability ellipsoids.

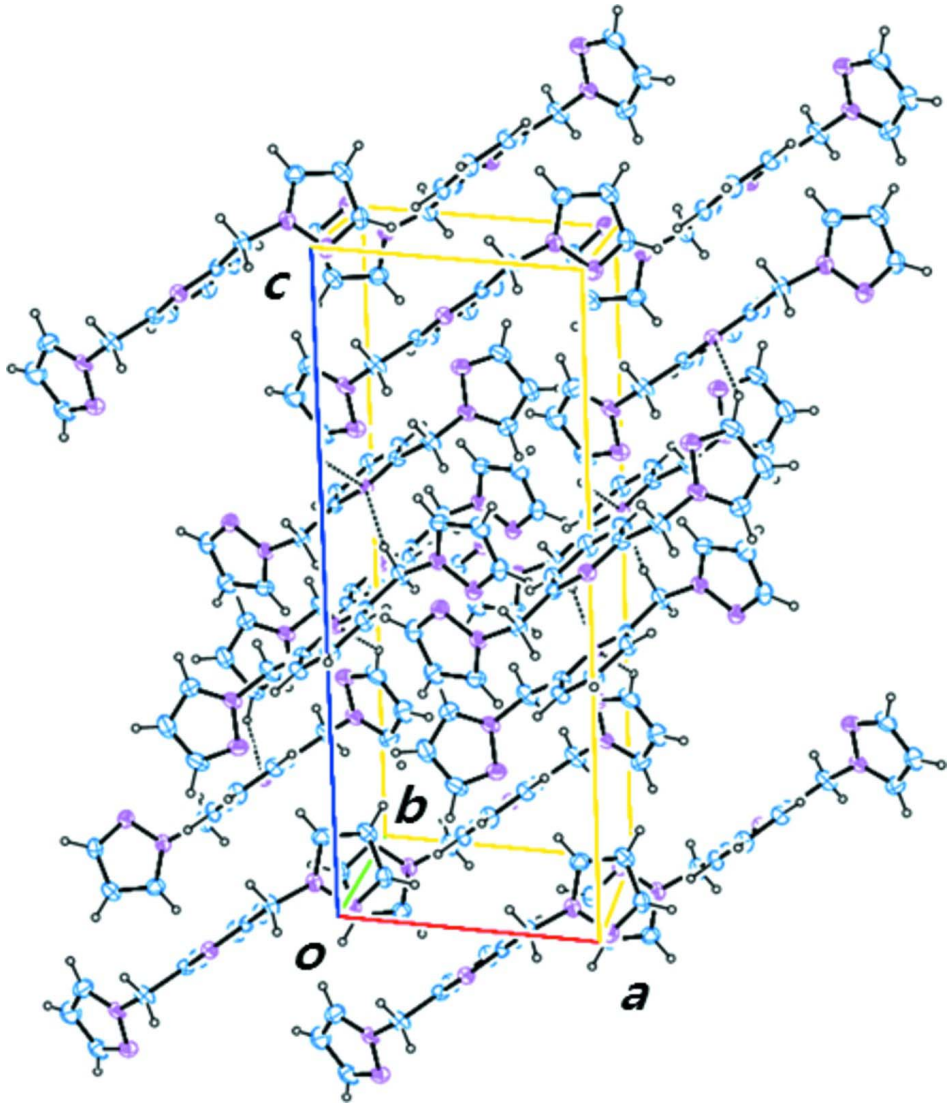

Figure 2

Part of the crystal structure of the title compound, showing molecules linked by intermolecular C—H···N hydrogen bonds (dashed lines).

2,6-Bis[(1*H*-pyrazol-1-yl)methyl]pyridine

Crystal data

$C_{13}H_{13}N_5$
$M_r = 239.28$
Monoclinic, $P2_1/n$
Hall symbol: -P 2yn
$a = 7.481\ (3)$ Å
$b = 9.076\ (4)$ Å
$c = 19.021\ (8)$ Å
$\beta = 95.471\ (5)°$
$V = 1285.7\ (9)$ Å^3
$Z = 4$

$F(000) = 504$
$D_x = 1.236$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 5271 reflections
$\theta = 2.2–25.5°$
$\mu = 0.08$ mm^{-1}
$T = 296$ K
Block, colourless
0.26 × 0.2 × 0.15 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Radiation source: fine-focus sealed tube
φ and ω scans
25319 measured reflections
3136 independent reflections
2260 reflections with $I > 2\sigma(I)$
$R_{int} = 0.040$
$\theta_{max} = 28.2°$, $\theta_{min} = 2.2°$
$h = -9 \rightarrow 9$
$k = -12 \rightarrow 12$
$l = -25 \rightarrow 25$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.060$
$wR(F^2) = 0.149$
$S = 1.09$
3136 reflections
163 parameters
0 restraints
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0539P)^2 + 0.4331P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.24$ e Å^{-3}
$\Delta\rho_{min} = -0.28$ e Å^{-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 (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
N1	−0.0152 (2)	0.79070 (17)	0.01406 (8)	0.0502 (4)
C2	−0.1286 (3)	0.7141 (2)	−0.02875 (11)	0.0576 (5)
H2	−0.2403	0.6823	−0.0172	0.069*
C3	−0.0626 (3)	0.6867 (2)	−0.09235 (11)	0.0637 (6)
H3	−0.1184	0.6351	−0.1306	0.076*
C4	0.1019 (3)	0.7512 (2)	−0.08738 (10)	0.0569 (5)
H4	0.1821	0.7522	−0.1218	0.068*
N5	0.12629 (18)	0.81324 (15)	−0.02326 (8)	0.0438 (4)
C6	0.2836 (2)	0.88545 (19)	0.01027 (11)	0.0529 (5)
H6A	0.2458	0.9661	0.0388	0.063*
H6B	0.3512	0.9272	−0.026	0.063*
C7	0.4057 (2)	0.78510 (17)	0.05647 (9)	0.0382 (4)
C8	0.3819 (2)	0.63422 (19)	0.05958 (10)	0.0481 (4)
H8	0.2873	0.5885	0.0327	0.058*
C9	0.5017 (2)	0.5534 (2)	0.10339 (10)	0.0544 (5)
H9	0.4889	0.4517	0.1065	0.065*
C10	0.6403 (2)	0.62335 (19)	0.14246 (9)	0.0497 (4)
H10	0.7221	0.5703	0.1724	0.06*
C11	0.6554 (2)	0.77450 (18)	0.13620 (8)	0.0424 (4)
N12	0.53963 (18)	0.85448 (15)	0.09409 (7)	0.0402 (3)
C13	0.8035 (3)	0.8643 (2)	0.17501 (11)	0.0619 (5)
H13A	0.8628	0.9211	0.1408	0.074*
H13B	0.7503	0.9334	0.2059	0.074*

N14	0.9367 (2)	0.77839 (17)	0.21661 (8)	0.0504 (4)
N15	0.9129 (2)	0.7377 (2)	0.28293 (8)	0.0620 (5)
C16	1.0538 (3)	0.6541 (3)	0.30142 (12)	0.0687 (6)
H16	1.0754	0.61	0.3455	0.082*
C17	1.1637 (3)	0.6396 (3)	0.24904 (14)	0.0860 (8)
H17	1.2698	0.5859	0.25	0.103*
C18	1.0849 (3)	0.7199 (3)	0.19552 (12)	0.0785 (7)
H18	1.1269	0.7323	0.1514	0.094*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0469 (8)	0.0497 (9)	0.0545 (9)	−0.0040 (7)	0.0074 (7)	0.0014 (7)
C2	0.0445 (10)	0.0549 (11)	0.0728 (13)	−0.0086 (9)	0.0029 (9)	−0.0026 (10)
C3	0.0622 (13)	0.0643 (13)	0.0615 (13)	−0.0056 (10)	−0.0110 (10)	−0.0094 (10)
C4	0.0613 (12)	0.0639 (12)	0.0458 (10)	0.0064 (10)	0.0063 (9)	0.0065 (9)
N5	0.0406 (7)	0.0410 (8)	0.0486 (8)	−0.0031 (6)	−0.0016 (6)	0.0103 (6)
C6	0.0475 (10)	0.0387 (9)	0.0696 (12)	−0.0087 (8)	−0.0093 (9)	0.0157 (8)
C7	0.0357 (8)	0.0361 (8)	0.0435 (9)	−0.0018 (6)	0.0068 (7)	0.0050 (7)
C8	0.0437 (9)	0.0375 (9)	0.0616 (11)	−0.0065 (7)	−0.0034 (8)	0.0042 (8)
C9	0.0583 (11)	0.0314 (8)	0.0721 (13)	−0.0021 (8)	−0.0015 (9)	0.0070 (8)
C10	0.0550 (11)	0.0414 (9)	0.0512 (10)	0.0062 (8)	−0.0033 (8)	0.0083 (8)
C11	0.0476 (9)	0.0409 (9)	0.0385 (8)	0.0012 (7)	0.0025 (7)	0.0003 (7)
N12	0.0441 (8)	0.0340 (7)	0.0419 (7)	−0.0017 (6)	0.0015 (6)	0.0032 (6)
C13	0.0706 (13)	0.0468 (11)	0.0633 (12)	−0.0017 (9)	−0.0204 (10)	−0.0002 (9)
N14	0.0540 (9)	0.0551 (9)	0.0396 (8)	−0.0044 (7)	−0.0075 (7)	0.0015 (7)
N15	0.0639 (10)	0.0806 (12)	0.0411 (9)	−0.0067 (9)	0.0033 (8)	0.0023 (8)
C16	0.0755 (14)	0.0739 (14)	0.0521 (12)	−0.0096 (12)	−0.0173 (11)	0.0148 (11)
C17	0.0613 (14)	0.115 (2)	0.0787 (17)	0.0220 (14)	−0.0098 (13)	0.0017 (15)
C18	0.0617 (13)	0.121 (2)	0.0539 (13)	0.0083 (14)	0.0119 (11)	0.0059 (13)

Geometric parameters (Å, º)

N1—C2	1.317 (2)	C9—H9	0.93
N1—N5	1.345 (2)	C10—C11	1.383 (2)
C2—C3	1.372 (3)	C10—H10	0.93
C2—H2	0.93	C11—N12	1.336 (2)
C3—C4	1.358 (3)	C11—C13	1.511 (2)
C3—H3	0.93	C13—N14	1.441 (2)
C4—N5	1.340 (2)	C13—H13A	0.97
C4—H4	0.93	C13—H13B	0.97
N5—C6	1.442 (2)	N14—C18	1.326 (3)
C6—C7	1.511 (2)	N14—N15	1.343 (2)
C6—H6A	0.97	N15—C16	1.319 (3)
C6—H6B	0.97	C16—C17	1.357 (3)
C7—N12	1.332 (2)	C16—H16	0.93
C7—C8	1.383 (2)	C17—C18	1.342 (3)
C8—C9	1.376 (2)	C17—H17	0.93

C8—H8	0.93	C18—H18	0.93
C9—C10	1.372 (2)		
C2—N1—N5	104.28 (15)	C8—C9—H9	120.1
N1—C2—C3	112.10 (18)	C9—C10—C11	118.44 (16)
N1—C2—H2	123.9	C9—C10—H10	120.8
C3—C2—H2	123.9	C11—C10—H10	120.8
C4—C3—C2	105.09 (18)	N12—C11—C10	122.49 (16)
C4—C3—H3	127.5	N12—C11—C13	113.78 (15)
C2—C3—H3	127.5	C10—C11—C13	123.73 (16)
N5—C4—C3	106.77 (18)	C7—N12—C11	118.43 (14)
N5—C4—H4	126.6	N14—C13—C11	114.41 (16)
C3—C4—H4	126.6	N14—C13—H13A	108.7
C4—N5—N1	111.76 (15)	C11—C13—H13A	108.7
C4—N5—C6	128.93 (17)	N14—C13—H13B	108.7
N1—N5—C6	119.07 (15)	C11—C13—H13B	108.7
N5—C6—C7	113.96 (14)	H13A—C13—H13B	107.6
N5—C6—H6A	108.8	C18—N14—N15	111.34 (17)
C7—C6—H6A	108.8	C18—N14—C13	127.23 (18)
N5—C6—H6B	108.8	N15—N14—C13	121.22 (17)
C7—C6—H6B	108.8	C16—N15—N14	103.57 (17)
H6A—C6—H6B	107.7	N15—C16—C17	112.7 (2)
N12—C7—C8	122.57 (15)	N15—C16—H16	123.7
N12—C7—C6	114.16 (14)	C17—C16—H16	123.7
C8—C7—C6	123.27 (15)	C18—C17—C16	104.5 (2)
C9—C8—C7	118.33 (16)	C18—C17—H17	127.7
C9—C8—H8	120.8	C16—C17—H17	127.7
C7—C8—H8	120.8	N14—C18—C17	107.9 (2)
C10—C9—C8	119.73 (16)	N14—C18—H18	126
C10—C9—H9	120.1	C17—C18—H18	126

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C4—H4···N15^{i}	0.93	2.62	3.550 (3)	178
C6—H6*B*···N12^{ii}	0.97	2.54	3.430 (2)	152

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