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(2*S**,5*R**)-2,5-Dimethyl-1,4-bis(pyridin-2-ylmethyl)piperazine

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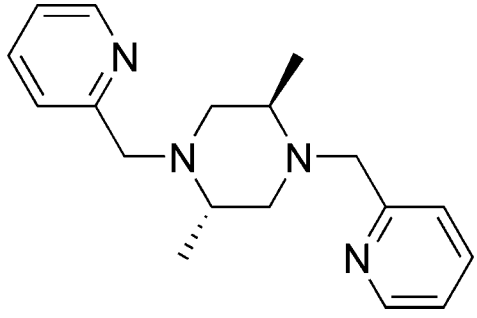
Key indicators: single-crystal X-ray study; T = 173 K; mean σ(C–C) = 0.002 Å; R factor = 0.044; wR factor = 0.131; data-to-parameter ratio = 15.1.

The title compound, $C_{18}H_{24}N_4$, resides on a crystallographic inversion centre, so that the asymmetric unit comprises one half-molecule. The piperazine ring adopts a chair conformation, with the mean planes of the two equatorial pyridine rings parallel to each other and separated by 2.54 (3) Å. No classical hydrogen bonds are observed.

Related literature

For related work on the synthesis of tetradentate pyridine-piperazine ligands and for metal complexes of these ligands, see: Geiger *et al.* (2011); Ostermeier *et al.* (2006, 2009); Nam (2007); Huuskonen *et al.* (1995); Que & Tolman (2008); Ratilainen *et al.* (1999); Fuji *et al.* (1996). For the synthesis, see: Halfen *et al.* (2000).



Experimental

Crystal data

$C_{18}H_{24}N_4$
M_r = 296.41
Orthorhombic, *Pbca*
a = 9.4097 (5) Å
b = 9.2191 (5) Å
c = 18.7473 (9) Å
V = 1626.29 (14) Å^3
Z = 4
Cu $K\alpha$ radiation
μ = 0.57 mm^{-1}
T = 173 K
0.22 × 0.18 × 0.04 mm

Data collection

Agilent Xcalibur (Eos, Gemini) diffractometer
Absorption correction: multi-scan (*CrysAlis PRO* and *CrysAlis RED*; Agilent, 2012)
T_{min} = 0.817, T_{max} = 1.000
10101 measured reflections
1545 independent reflections
1392 reflections with $I > 2\sigma(I)$
R_{int} = 0.064

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.044
$wR(F^2)$ = 0.131
S = 1.07
1545 reflections
102 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.24 e Å^{-3}
$\Delta\rho_{min}$ = −0.19 e Å^{-3}

Data collection: *CrysAlis PRO* (Agilent, 2012); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis RED* (Agilent, 2012); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2012* (Sheldrick, 2008); molecular graphics: *OLEX2* (Dolomanov *et al.*, 2009); software used to prepare material for publication: *OLEX2*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: FJ2633).

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(2*S**,5*R**)-2,5-Dimethyl-1,4-bis(pyridin-2-ylmethyl)piperazine

Christopher Goh, Lilliana S. Morris, Michael P. Girouard, Tamuka Chidanguro and Jerry P. Jasinski

S1. Comment

Multidentate ligands containing pyridine and amine donor moieties have applications in metal-catalyzed oxidations and in the design of macrocyclic metal-binding receptors. Examples include the manganese, iron, and copper complexes of tetradentate pyridine and amine ligands for biologically-inspired oxidations (Geiger *et al.*, 2011; Ostermeier *et al.*, 2009; Que *et al.*, 2008; Nam, 2007; Ostermeier *et al.*, 2006), copper complexes of pyridine-diazacycloalkanes as catalysts for the aziridination of alkenes (Halfen *et al.*, 2000) and macrocyclic piperazinacyclophanes as complexation agents for a host of metals (Ratilainen *et al.*, 1999; Fuji *et al.*, 1996; Huuskonen *et al.*, 1995). Our group has been interested in the use of neutral tetradentate hetero-aromatic-amine ligands in metal-catalyzed oxidations. Here we report the synthesis and crystal structure of the meso form of the tetradentate ligand, (I), (2S,5R)-2,5-dimethyl-1,4-bis(pyridin-2-ylmethyl)-piperazine (Fig. 1).

In the asymmetric unit of the title compound, $C_{18}H_{24}N_4$, (I), a piperazine ring (N1/C2/C3A/N1A/C2A/C3) is formed by a center of symmetry connecting each half (N/C/C) to a methyl group and pyridine ring at the 2,5 and 1,4 positions, respectively. The piperazine ring adopts a chair conformation with puckering parameters Q = 0.5804 (13)Å, θ = 0.00 (1)°, φ = 0.0000°. The mean planes of the two equatorial pyridine rings are parallel to each other and separated by 2.54 (3)Å, respectively. In the formation of this neutral tetradentate hetero-aromatic-amine ligand no classical hydrogen bonds are observed (Fig. 2).

S2. Experimental

The title compound was synthesized under a dinitrogen atmosphere by modifications of a previously published protocol (Halfen *et al.*, 2000). 2-picolyl chloride hydrochloride (2.87 g, 17.5 mmol) and triethylamine (4.88 mL, 35.0 mmol) were added to a suspension of (2R, 5S)-2,5-dimethylpiperazine (1.00 g, 8.76 mmol) in 30 mL of acetonitrile to form a slurry. The mixture was allowed to stir for 48 hours at room temperature and then treated with 100 mL of 1 M sodium hydroxide. The product was extracted with three portions of 50 mL of CH_2Cl_2. The combined fractions were dried with $MgSO_4$, filtered and the solvent removed to yield the crude product as a brown solid. Further purification by column chromatography with a Biotage Isolera™ Flash Purification System using a silica cartridge and a gradient of ethyl acetate and a mixture of ethyl acetate/methanol/triethylamine (90/5/5), followed by solvent removal yielded the pure product as a faintly brown transparent solid (1.40 g, 54% yield). Crystallization by evaporation from a concentrated diethyl ether solution led to isolation of crystals suitable for X-ray analysis (m.p.: 405–406K).

S3. Refinement

All of the H atoms were placed in their calculated positions and then refined using the riding model with Atom—H lengths of 0.95Å (CH), 0.99Å (CH_2) or 0.98Å (CH_3). Isotropic displacement parameters for these atoms were set to 1.2

(CH, CH_2) or 1.5 (CH_3times U_{eq} of the parent atom. Ternary CH were refined with riding coordinates: C2(H2), secondary CH_2 refined with riding coordinates: C3(H3A,H3B), C4(H4A,H4B), aromatic/amide H refined with riding coordinates: C6(H6), C7(H7), C8(H8), C9(H9), idealised Me refined as rotating group: C1(H1A,H1B,H1C).

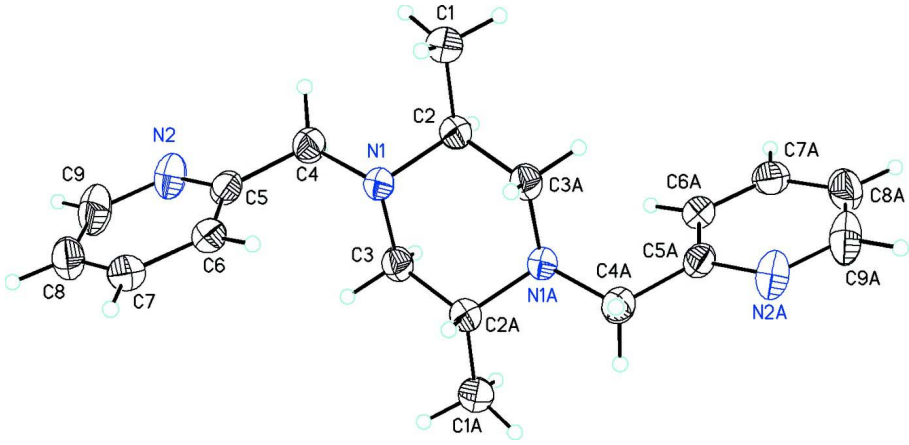

Figure 1

Molecular structure of the title compound showing the atom labeling scheme and 30% probability displacement ellipsoids.

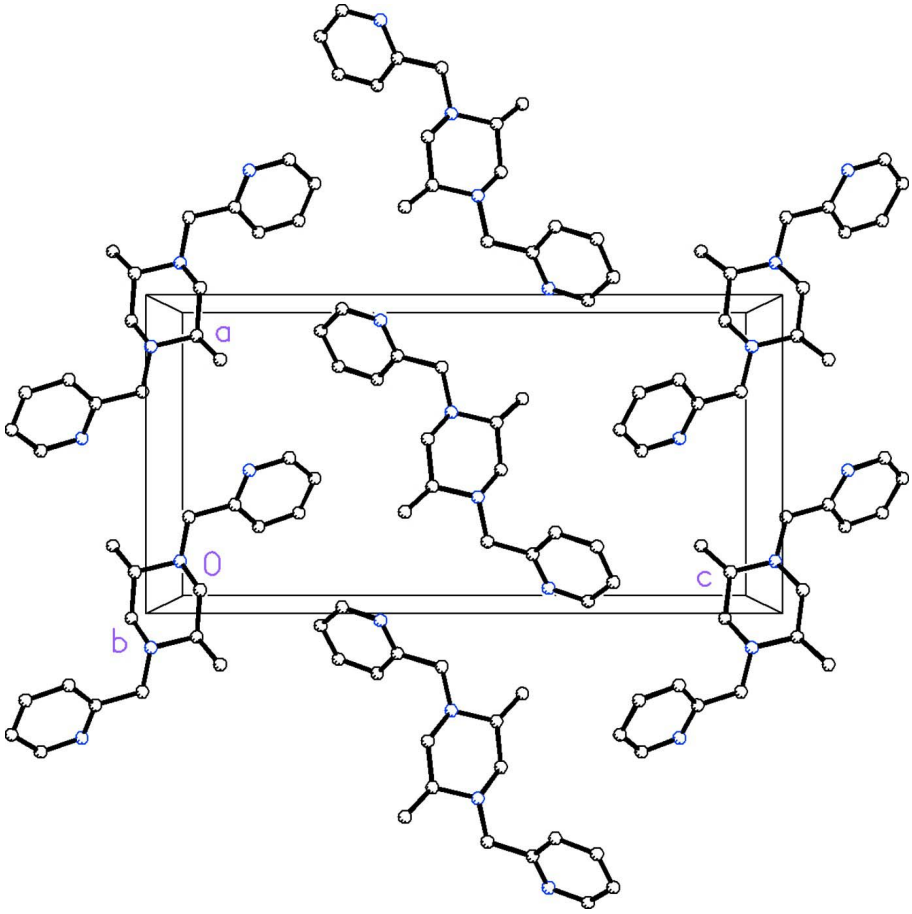

Figure 2

Packing diagram of the title compound viewed along the *b* axis. H atoms have been removed for clarity.

(2*S,5*R**)-2,5-Dimethyl-1,4-bis(pyridin-2-ylmethyl)piperazine**

Crystal data

$C_{18}H_{24}N_4$
$M_r = 296.41$
Orthorhombic, *Pbca*
$a = 9.4097$ (5) Å
$b = 9.2191$ (5) Å
$c = 18.7473$ (9) Å
$V = 1626.29$ (14) Å^3
$Z = 4$
$F(000) = 640$
$D_x = 1.211$ Mg m^{-3}
Cu $K\alpha$ radiation, $\lambda = 1.5418$ Å
Cell parameters from 4359 reflections
$\theta = 4.7$–$70.6°$
$\mu = 0.57$ mm^{-1}
$T = 173$ K
Block, colourless
0.22 × 0.18 × 0.04 mm

Data collection

Agilent Xcalibur (Eos, Gemini) diffractometer
Radiation source: Enhance (Cu) X-ray Source
Graphite monochromator
Detector resolution: 16.0416 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (*CrysAlis PRO* and *CrysAlis RED*; Agilent, 2012)
$T_{min} = 0.817$, $T_{max} = 1.000$
10101 measured reflections
1545 independent reflections
1392 reflections with $I > 2\sigma(I)$
$R_{int} = 0.064$
$\theta_{max} = 70.7°$, $\theta_{min} = 6.7°$
$h = -10 \rightarrow 11$
$k = -8 \rightarrow 11$
$l = -22 \rightarrow 21$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.044$
$wR(F^2) = 0.131$
$S = 1.07$
1545 reflections
102 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0744P)^2 + 0.3744P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.24$ e Å^{-3}
$\Delta\rho_{min} = -0.19$ e Å^{-3}
Extinction correction: *SHELXL2012* (Sheldrick, 2008), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.0056 (9)

Special details

Experimental. ^{1}H-NMR ($CDCl_3$, 298 K): δ 8.55 (d, J = 3.5 Hz, 2H, py), 7.65 (m, 2H, py), 7.44 (d, J = 7.5 Hz, 2H, py), 7.15 (m, 2H, py), 4.15 (d, J = 14 Hz, 2 H, py-CH_2N), 3.38 (d, J = 14 Hz, 2H, py-CH_2N), 2.68 (m, 2H, NCH_2), 2.50 (m, 2H, NCH), 2.14 (m, 2H, NCH_2), 1.07 (d, J = 6.1 Hz, 6H, CH_3) ppm. ^{13}C-NMR ($CDCl_3$, 298K): δ 159.6 (py), 150.0 (py), 136.3 (py), 123.2 (py), 121.8 (py), 60.5, 59.7, 56.0, 17.8 (CH_3) ppm. MS: m/z 204 (py-$CH_2N_2C_6H_{12}$), m/z 175 (py-$CH_2NC_5H_9$), m/z 149 (py-$CH_2NC_3H_7$), m/z 135.0 (py-$CH_2NC_2H_4$), m/z 112 ($N_2C_6H_{12}$), m/z 93 (py-CH_3).

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.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
N1	0.35844 (11)	0.53852 (12)	0.52226 (5)	0.0296 (3)
N2	0.05342 (13)	0.49301 (14)	0.64052 (7)	0.0433 (4)
C1	0.31099 (16)	0.64089 (18)	0.40179 (8)	0.0431 (4)
H1A	0.3227	0.7380	0.4222	0.065*
H1B	0.2100	0.6148	0.4018	0.065*
H1C	0.3469	0.6403	0.3527	0.065*
C2	0.39382 (14)	0.53155 (14)	0.44625 (7)	0.0309 (4)
H2	0.3740	0.4316	0.4281	0.037*
C3	0.44872 (13)	0.43666 (15)	0.56137 (7)	0.0316 (4)
H3A	0.4297	0.3372	0.5439	0.038*
H3B	0.4230	0.4399	0.6126	0.038*
C4	0.20889 (13)	0.50891 (17)	0.53835 (7)	0.0352 (4)
H4A	0.1907	0.4036	0.5333	0.042*
H4B	0.1482	0.5604	0.5034	0.042*
C5	0.16893 (14)	0.55639 (15)	0.61287 (7)	0.0319 (3)
C6	0.24476 (15)	0.66281 (16)	0.64872 (7)	0.0339 (4)
H6	0.3263	0.7057	0.6275	0.041*
C7	0.20015 (15)	0.70565 (18)	0.71574 (7)	0.0411 (4)
H7	0.2508	0.7779	0.7414	0.049*
C8	0.08112 (17)	0.64193 (19)	0.74468 (8)	0.0476 (4)
H8	0.0476	0.6693	0.7905	0.057*
C9	0.01202 (18)	0.53765 (18)	0.70546 (9)	0.0507 (5)
H9	−0.0704	0.4943	0.7256	0.061*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0247 (6)	0.0370 (6)	0.0270 (6)	0.0004 (4)	0.0020 (4)	0.0000 (4)
N2	0.0353 (7)	0.0432 (7)	0.0513 (8)	−0.0014 (5)	0.0150 (5)	−0.0023 (6)
C1	0.0377 (8)	0.0577 (10)	0.0340 (7)	0.0097 (7)	0.0010 (6)	0.0065 (6)
C2	0.0296 (7)	0.0365 (7)	0.0266 (7)	0.0013 (5)	0.0006 (5)	−0.0020 (5)
C3	0.0315 (7)	0.0345 (7)	0.0288 (7)	−0.0004 (5)	0.0043 (5)	0.0021 (5)
C4	0.0268 (7)	0.0452 (8)	0.0335 (7)	−0.0029 (5)	0.0015 (5)	−0.0039 (6)
C5	0.0253 (6)	0.0356 (7)	0.0347 (7)	0.0050 (5)	0.0028 (5)	0.0033 (5)
C6	0.0279 (7)	0.0420 (8)	0.0317 (7)	0.0033 (5)	−0.0001 (5)	0.0019 (5)
C7	0.0380 (8)	0.0503 (9)	0.0349 (7)	0.0098 (6)	−0.0043 (6)	−0.0040 (6)
C8	0.0485 (9)	0.0590 (10)	0.0353 (8)	0.0155 (7)	0.0111 (6)	0.0009 (7)
C9	0.0447 (9)	0.0509 (10)	0.0566 (10)	0.0024 (7)	0.0245 (8)	0.0042 (8)

Geometric parameters (Å, º)

N1—C2	1.4648 (16)	C3—H3B	0.9900
N1—C3	1.4633 (17)	C4—H4A	0.9900
N1—C4	1.4649 (17)	C4—H4B	0.9900
N2—C5	1.3385 (18)	C4—C5	1.5115 (18)

N2—C9	1.343 (2)	C5—C6	1.387 (2)
C1—H1A	0.9800	C6—H6	0.9500
C1—H1B	0.9800	C6—C7	1.3824 (19)
C1—H1C	0.9800	C7—H7	0.9500
C1—C2	1.5226 (19)	C7—C8	1.376 (2)
C2—H2	1.0000	C8—H8	0.9500
C2—C3^{i}	1.5171 (17)	C8—C9	1.374 (3)
C3—C2^{i}	1.5171 (17)	C9—H9	0.9500
C3—H3A	0.9900		

C2—N1—C4	114.24 (10)	N1—C4—H4A	109.2
C3—N1—C2	109.11 (10)	N1—C4—H4B	109.2
C3—N1—C4	109.57 (10)	N1—C4—C5	112.04 (11)
C5—N2—C9	116.93 (14)	H4A—C4—H4B	107.9
H1A—C1—H1B	109.5	C5—C4—H4A	109.2
H1A—C1—H1C	109.5	C5—C4—H4B	109.2
H1B—C1—H1C	109.5	N2—C5—C4	115.69 (12)
C2—C1—H1A	109.5	N2—C5—C6	122.62 (13)
C2—C1—H1B	109.5	C6—C5—C4	121.65 (12)
C2—C1—H1C	109.5	C5—C6—H6	120.4
N1—C2—C1	112.78 (11)	C7—C6—C5	119.10 (13)
N1—C2—H2	109.2	C7—C6—H6	120.4
N1—C2—C3^{i}	107.77 (10)	C6—C7—H7	120.5
C1—C2—H2	109.2	C8—C7—C6	118.91 (14)
C3^{i}—C2—C1	108.69 (11)	C8—C7—H7	120.5
C3^{i}—C2—H2	109.2	C7—C8—H8	120.9
N1—C3—C2^{i}	113.32 (11)	C9—C8—C7	118.22 (14)
N1—C3—H3A	108.9	C9—C8—H8	120.9
N1—C3—H3B	108.9	N2—C9—C8	124.22 (15)
C2^{i}—C3—H3A	108.9	N2—C9—H9	117.9
C2^{i}—C3—H3B	108.9	C8—C9—H9	117.9
H3A—C3—H3B	107.7		

N1—C4—C5—N2	−158.76 (12)	C4—N1—C2—C3^{i}	−179.58 (11)
N1—C4—C5—C6	23.55 (18)	C4—N1—C3—C2^{i}	−174.32 (11)
N2—C5—C6—C7	0.1 (2)	C4—C5—C6—C7	177.62 (12)
C2—N1—C3—C2^{i}	59.93 (15)	C5—N2—C9—C8	−0.6 (3)
C2—N1—C4—C5	−164.47 (11)	C5—C6—C7—C8	−0.4 (2)
C3—N1—C2—C1	−176.54 (12)	C6—C7—C8—C9	0.2 (2)
C3—N1—C2—C3^{i}	−56.57 (14)	C7—C8—C9—N2	0.3 (3)
C3—N1—C4—C5	72.78 (14)	C9—N2—C5—C4	−177.26 (13)
C4—N1—C2—C1	60.45 (15)	C9—N2—C5—C6	0.4 (2)

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