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2,6-Bis(3,4,5-trimethylpyrazol-1-ylmethyl)pyridine

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Key indicators

Single-crystal X-ray study
T = 298 K
Mean σ(C–C) = 0.009 Å
R factor = 0.094
wR factor = 0.295
Data-to-parameter ratio = 15.0

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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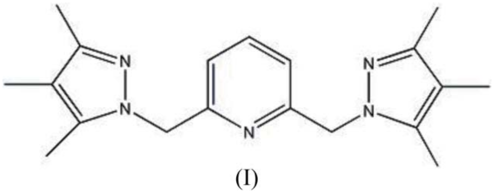
The title compound, $C_{19}H_{25}N_5$, adopts pseudo-C_2 symmetry in which the non-substituted N atoms of the pyrazole rings are on opposite sides of the pyridine plane. The packing involves C—H$\cdots\pi$, π–π, C—H$\cdots$N and hydrophobic $CH_3\cdots CH_3$ interactions, which are responsible for the observed columnar arrangement.

Comment

The development of new ligands bearing donor atoms other than phosphorus, in particular nitrogen-containing heterocyclic units, has been receiving increasing interest in the coordination chemistry of transition-metal-based homogeneous catalysis (Togni & Venanzi, 1994; Nishiyama *et al.*, 1991). In this context, the planar tridentate ligand 2,6-bis(imino)pyridine and its derivatives have attracted great attention in the past few years, owing to their versatile coordination properties that point toward new catalytic applications (Abel *et al.*, 1994; Orrell *et al.*, 1997). Iron(II) and cobalt(II) complexes containing voluminous aryl-substituted bis(imino)pyridine ligands were developed by the Brookhardt (Small *et al.*, 1998) and Gibson groups (Britovsek *et al.*, 1998). Both families of complexes exhibit a very high activity for olefin polymerization. It has also been reported that bis(imino)pyridine–ruthenium(II) complexes can catalyse the epoxidation of olefins (Cetinkaya *et al.*, 1999). The discovery of this class of olefin polymerization catalysts has provided a great incentive to seek polymerization systems based on the late transition metals (Rieger *et al.*, 2003).



(I)

During the past decade, the synthesis of a new family of tridentate planar ligands based on 2,6-bis(*N*-pyrazolyl)pyridine has been reported. The interest in involving pyrazole rings arises from their ease of tailoring to meet specific electronic and/or steric effects. These ligands are also structural analogues to 2,2′:6′,2″-terpyridine; however, the substituents on the pyrazole rings can be easily varied. For example, a fine control of the redox potential of Ru^{III}/Ru^{II} is available with differing number of methyl groups on the pyrazole ring (Jameson *et al.*, 1989). Another family of tridentate *N*-donor ligands corresponds to 2,6-bis(pyrazol-1-ylmethyl)pyridine. After coordination and as a result of the

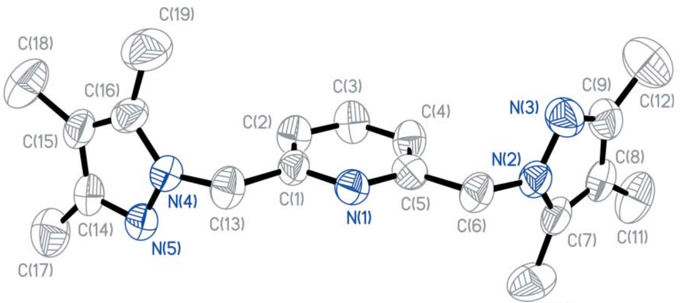


Figure 1
A view of the molecule of (I), showing the atom-labelling scheme. Displacement parameter are drawn at the 50% probability level. H atoms have been omitted for clarity.

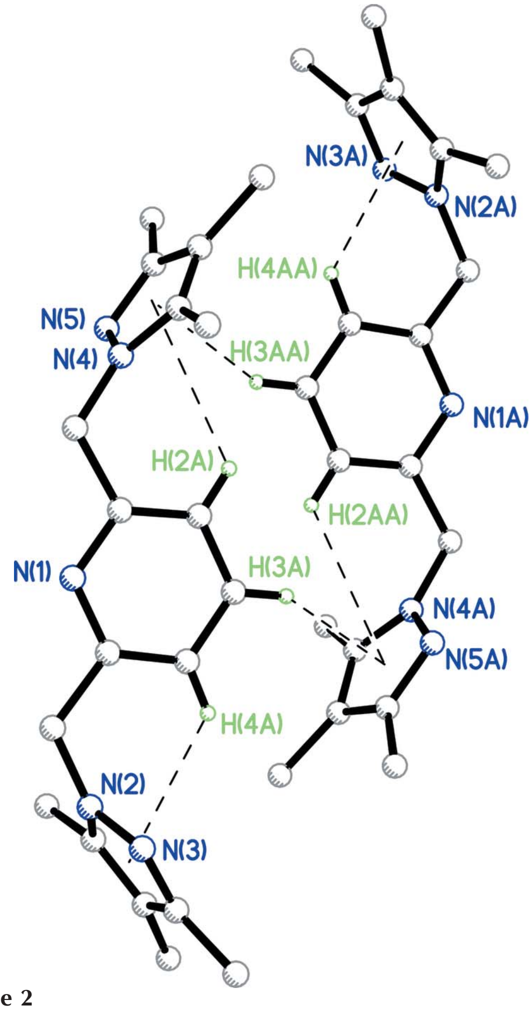
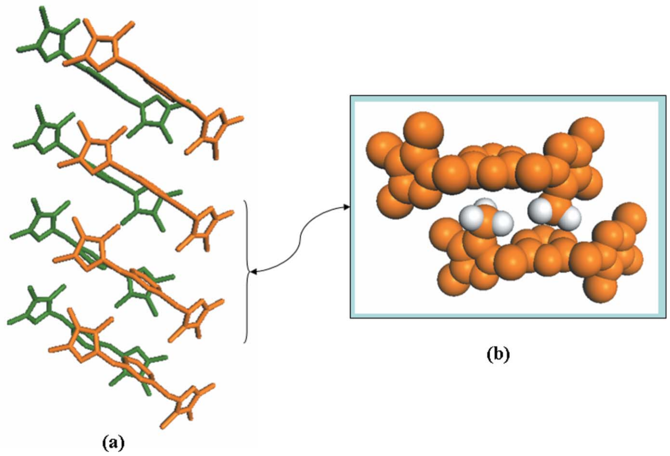


Figure 2
Ball-and-stick representation of the discrete bimolecular self-assembly found in the crystal structure of (I). C—H$\cdots\pi$ Interactions are shown as dashed lines. H atoms, other than those involved in these interactions, have been omitted for clarity.

presence of methylene groups, these molecules adopt a non-planar conformation in which the electronic conjugation between pyrazole and pyridine rings is prevented. Mukherjee's group (Singh *et al.*, 2003) has developed a very rich coordination chemistry with non-planar tridentate and bidentate pyrazole–pyridine systems. We report here the synthesis and crystal structure of a member of this family, namely 2,6-bis(3,4,5-trimethylpyrazol-1-ylmethyl)pyridine, (I). Knowledge of the molecular structure offers the possibility of comparing directly structural parameters of the free and coordinated pyrazole–pyridine.


(b)

(a)

Figure 3
Views of the packing of (I) showing (*a*) a column extending along the *a* axis, and (*b*) a representation of two molecules displaying the $CH_3\cdots\pi$ interactions found in the columns. Only the methyl H atoms involved in C—H$\cdots\pi$ interactions are shown.

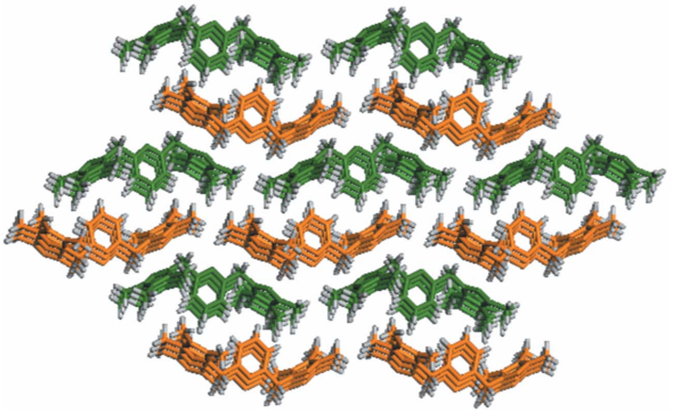


Figure 4
The columnar stacking in (I), viewed along the *a* axis.

The molecule adopts pseudo-C_2 symmetry (Fig. 1) in which the non-substituted N atoms of the pyrazole rings are on opposite sides of the pyridine plane. The dihedral angle between the mean planes through the N2/N3/C7–C9 (N2–C9) and N4/N5/C14–C16 (N4–C16) pyrazole rings is 69.2 (2)°. These rings are nearly orthogonal to the pyridine ring, the dihedral angles they form being 92.2 (2) and 96.4 (2)°, respectively. In this conformation, two intramolecular C—H$\cdots\pi$ interactions (Fig. 2) involving both *ortho* C atoms of the pyridine ring and the π-electron cloud of the pyrazole units are observed ($H4a\cdots Cg1 = 2.71$ Å and $C4—H4a\cdots Cg1 = 125.4°$; $H\cdots Cg2 = 3.00$ Å and $C2—H2a\cdots Cg2 = 121.4°$; *Cg*1 and *Cg*2 are the centroids of the N2–C9 and N4–C16 rings, respectively).

The roughly concave shape adopted by (I) allows a centrosymmetric head-to-tail arrangement between two neighbouring molecules, which is predominately sustained by intermolecular C—H$\cdots\pi$ interactions (Fig. 2), involving the *para* C atom of the pyridine ring and the N4–C16 pyrazole ring [H3*a*$\cdots$*Cg*2^{i} = 2.95 Å and C3—H3*a*$\cdots$*Cg*2^{i} = 146.3°; symmetry code: (i) $1 - x, 1 - y, 1 - z$]. A hydrophobic methyl–methyl interaction [C11$\cdots$C18^{i} = 3.855 (10) Å] is present. This assembly generates columnar stacking along the *a* axis (Fig. 3*a*) by means of two $CH_3\cdots\pi$ interactions (Fig. 3*b*) in which the π-electron density corresponds to the pyridine ring [C10$^{ii}\cdots$*Cg*3 = 3.43 Å and C19$\cdots$*Cg*3^{ii} = 3.67 Å; *Cg*3 is the centroid of the pyridine ring; symmetry code: (ii) $1 + x, y, z$]. The columns are linked by a π–π interaction between the pyrazole rings of neighbouring molecules [*Cg*2$\cdots$*Cg*1^{iii} = 4.26 Å; symmetry code: (iii) $1 + x, \frac{1}{2} - y, 2 + z$], and two C—H$\cdots$N hydrogen bonds in which the donor is attached to the methylene groups (Table 2). The crystal packing is otherwise dominated by hydrophobic methyl–methyl interactions (Fig. 4).

Experimental

Under a nitrogen atmosphere, 3,4,5-trimethylpyrazole (2.20 g, 0.02 mol) was added slowly to a suspension of NaH (0.48 g, 0.02 mol) in tetrahydrofuran (50 ml). The suspension was stirred at room temperature for 1 h, followed by the slow addition of 2,6-bis(chloromethyl)pyridine (1.76 g, 0.01 mol) in tetrahydrofuran (20 ml). The mixture was stirred overnight and filtered through celite. The filtrate was evacuated to dryness and the crude product was recrystallized from CH_2Cl_2–hexane (1:1 (*v*/*v*) at 263 K (yield: 2.42 g, 75%; m.p. 433 K). Elemental analysis found: C 69.94, H 7.62, N 21.48%; calculated for $C_{19}H_{25}N_5$: C 70.56, H 7.79, N 21.64%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.89 (*s*, 6H), 2.05 (*s*, 6H), 2.15 (*s*, 6H), 5.30 (*s*, 4H), 6.57 (*d, J* = 7.8 Hz, 2H), 7.76 (*t, J* = 7.8 Hz, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 8.1, 9.4, 11.8, 54.5, 112.0, 119.5, 136.4, 138.1, 146.8, 157.2.

Crystal data

$C_{19}H_{25}N_5$
$M_r = 323.44$
Monoclinic, $P2_1/c$
$a = 6.7834\ (14)$ Å
$b = 17.953\ (4)$ Å
$c = 15.247\ (3)$ Å
$\beta = 92.53\ (3)°$
$V = 1855.0\ (6)$ Å^3
$Z = 4$
$D_x = 1.158$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 19 reflections
$\theta = 7.3$–$16.5°$
$\mu = 0.07$ mm^{-1}
$T = 298\ (2)$ K
Irregular fragment, colourless
0.40 × 0.30 × 0.20 mm

Data collection

Rigaku AFC-7S diffractometer
ω–2θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{min} = 0.972$, $T_{max} = 0.986$
3547 measured reflections
3254 independent reflections
1223 reflections with $I > 2\sigma(I)$
$R_{int} = 0.130$
$\theta_{max} = 25.0°$
$h = 0 \rightarrow 8$
$k = 0 \rightarrow 21$
$l = -18 \rightarrow 18$
3 standard reflections every 150 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.094$
$wR(F^2) = 0.295$
$S = 0.99$
3254 reflections
217 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.1343P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.22$ e Å^{-3}
$\Delta\rho_{min} = -0.24$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

N1—C5	1.341 (6)	C1—C2	1.361 (8)
N1—C1	1.351 (7)	C1—C13	1.513 (7)
N2—N3	1.350 (6)	C2—C3	1.382 (8)
N2—C7	1.357 (7)	C3—C4	1.380 (8)
N2—C6	1.445 (6)	C4—C5	1.374 (8)
N3—C9	1.340 (7)	C5—C6	1.515 (7)
N4—N5	1.339 (6)	C7—C8	1.359 (8)
N4—C16	1.361 (7)	C8—C9	1.417 (8)
N4—C13	1.452 (7)	C14—C15	1.405 (8)
N5—C14	1.337 (7)	C15—C16	1.346 (8)
N3—N2—C6	118.9 (5)	C2—C1—C13	123.8 (6)
C7—N2—C6	128.0 (5)	N1—C5—C6	114.4 (5)
N5—N4—C13	119.1 (5)	N2—C6—C5	113.7 (5)
C16—N4—C13	128.9 (5)	N4—C13—C1	115.3 (5)
N1—C1—C13	113.5 (5)		

Table 2
Hydrogen-bond geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
C6—H6*a*$\cdots$N5^{i}	0.97	2.56	3.522 (8)	175
C13—H13*a*$\cdots$N3^{ii}	0.97	2.56	3.526 (8)	173

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

All H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms, with C—H distances of 0.93 (aromatic), 0.96 (methyl) and 0.97 Å (methylene), and with U_{iso}(H) = 1.5 (1.2 for aromatic H atoms) times U_{eq}(C). The size of the selected crystal was relatively small, lying in the lower limit for the four-circle diffractometer used. This, together with the nature of the atoms present in the structure, which involves only light C, N and H atoms, could account for the poor diffraction quality of the crystal, resulting in the small number of observed reflections and high R_{int}, weighted and unweighted R factors.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1993); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1999); program(s) used to solve structure: *SHELXTL-NT* (Bruker, 1998); program(s) used to refine structure: *SHELXTL-NT*; molecular graphics: *SHELXTL-NT*; software used to prepare material for publication: *SHELXTL-NT*.

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