3-(4-Pyridyl)-5-(2-pyridyl)-1*H*-pyrazole

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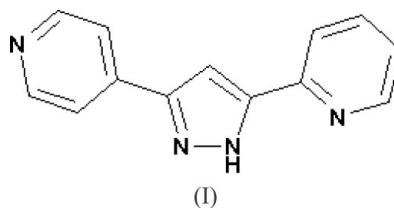
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The title compound, $C_{13}H_{10}N_4$, is a non-linear 2,4-bipyridyl-type ligand. Adjacent centrosymmetric molecules are linked together by pairs of intermolecular N—H···N hydrogen bonds. The dimers stack along the *b* axis.

Comment

The title compound, (I), is a non-linear 2,4-bipyridyl-type ligand that can be used as a zigzag-forming building unit in novel supramolecular architectures (Khlobystov *et al.*, 2001). Some contemporary results for novel coordination polymers based on closely related copper(II) and ruthenium(II) salts provide good reasons for future in-depth study (Pons *et al.*, 2001; Catalano & Craig, 2003). The synthesis and spectro-scopic data for (I) were previously described by Ferles *et al.* (1990). The molecule of (I) is planar within 0.115 (3) Å. The largest deviation is observed for the central methine C atom (C3) of the pyrazole ring. The dihedral angles formed by the 2-pyridine and 4-pyridine rings with the pyrazole fragment are 5.4 (2) and 2.8 (2)°, respectively. Adjacent centrosymmetric-ally related molecules (symmetry code: $1 - x$, $1 - y$, $1 - z$) are linked together by pairs of intermolecular N—H···N hydrogen bonds [2.18 (4) Å]. These dimers stack along the *b* axis (Fig. 2). The distance between the centroids of the pyra-zole rings of adjacent molecules in a stack (symmetry code: $1 - x$, $-y$, $1 - z$) is 3.572 (6) Å with an interplanar spacing of 3.546 (6) Å and a lateral centroid shift of 0.43 Å.

(I)

Experimental

Previously prepared 1-(2-pyridyl)-3-(4-pyridyl)propane-1,3-dione (1 g, 4.5 mmol; Ferles *et al.*, 1990) was heated under reflux with 4 ml (68 mmol) of hydrazine hydrate in 8 ml of methanol for 2 h. After cooling of the solution, colorless needles were collected by filtration, resulting in 500 mg (51% yield, m.p. 465 K) of (I). The melting point and analytical data are in good agreement with literature data. ^{1}H NMR (301 K, CDCl$_3$, δ): 7.24 (*s*, 1H, 4*H*-pyraz), 7.48 (*ddd*, 1H, ^3J = 7.4 Hz, ^3J = 4.9 Hz, ^4J = 1.1 Hz, H-py2), 7.63 (*s*, 1H, NH), 7.84 (*d*, 2H, ^3J = 6.6 Hz, 3,5-H-py4), 7.89 (*dt*, 1H, ^{3} = 7.4 Hz, ^4J = 1.8 Hz, 4H-py2), 8.19 (*d*, 1H, ^3J = 7.4 Hz, 3H-py2), 8.72 (*d*, 1H, ^3J = 4.9 Hz, 6H-py2), 8.78 (*d*, 2H, ^3J = 6.6 Hz, 2,6-H-py4). ^{13}C NMR (301 K, CDCl$_3$, δ): 153.5, 151.2, 150.4, 147.2, 146.8, 143.3, 140.1, 138.2, 123.2, 121.6, 120.0,

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113.2. IR (mineral oil; ν, cm^{-1}): 3360 (NH). UV (EtOH, λ, nm): 255 (s, aromatic), 370 (s, C=N).

Crystal data

$C_{13}H_{10}N_4$	$D_x = 1.376$ Mg m^{-3}
$M_r = 222.25$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 25
$a = 13.708$ (3) Å	reflections
$b = 5.545$ (9) Å	$\theta = 11$–12°
$c = 15.018$ (6) Å	$\mu = 0.09$ mm^{-1}
$\beta = 109.94$ (2)°	$T = 293$ (2) K
$V = 1073.1$ (18) Å^3	Block, colorless
$Z = 4$	$0.50 \times 0.30 \times 0.10$ mm

Data collection

Enraf–Nonius CAD-4 diffractometer	$\theta_{max} = 25.0°$
	$h = -16 \rightarrow 16$
ω scans	$k = -1 \rightarrow 6$
Absorption correction: none	$l = -3 \rightarrow 17$
2937 measured reflections	2 standard reflections
1880 independent reflections	frequency: 120 min
968 reflections with $I > 2\sigma(I)$	intensity decay: none
$R_{int} = 0.054$	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0926P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.054$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.153$	$(\Delta/\sigma)_{max} < 0.001$
$S = 0.94$	$\Delta\rho_{max} = 0.27$ e Å^{-3}
1880 reflections	$\Delta\rho_{min} = -0.24$ e Å^{-3}
195 parameters	Extinction correction: SHELXL97
All H-atom parameters refined	Extinction coefficient: 0.022 (5)

Table 1
Selected geometric parameters (Å, °).

N1—C15	1.329 (4)	C2—C3	1.401 (4)
N1—C11	1.345 (4)	C2—C21	1.461 (4)
N2—C23	1.342 (4)	C11—C12	1.387 (4)
N2—C25	1.345 (4)	C12—C13	1.363 (4)
N3—C2	1.338 (4)	C13—C14	1.370 (5)
N3—N4	1.343 (3)	C14—C15	1.379 (5)
N4—C1	1.356 (4)	C21—C24	1.391 (4)
N4—H4	0.95 (3)	C21—C22	1.398 (4)
C1—C3	1.369 (4)	C22—C23	1.368 (4)
C1—C11	1.459 (4)	C24—C25	1.367 (4)
C15—N1—C11	117.4 (3)	N1—C11—C1	115.5 (3)
C23—N2—C25	115.1 (3)	C12—C11—C1	122.4 (3)
C2—N3—N4	105.0 (2)	C13—C12—C11	119.2 (3)
N3—N4—C1	112.8 (2)	C12—C13—C14	119.3 (3)
N3—N4—H4	128 (2)	C13—C14—C15	118.4 (3)
C1—N4—H4	117 (2)	N1—C15—C14	123.5 (3)
N4—C1—C3	105.6 (3)	C24—C21—C22	116.4 (3)
N4—C1—C11	119.3 (3)	C24—C21—C2	122.1 (3)
C3—C1—C11	135.1 (3)	C22—C21—C2	121.5 (3)
N3—C2—C3	110.2 (2)	C23—C22—C21	119.2 (3)
N3—C2—C21	119.6 (2)	N2—C23—C22	124.9 (3)
C3—C2—C21	130.1 (3)	C25—C24—C21	120.0 (3)
C1—C3—C2	106.3 (3)	N2—C25—C24	124.2 (3)
N1—C11—C12	122.1 (3)		

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

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
N4—H4⋯N1	0.95 (3)	2.34 (3)	2.702 (3)	102 (2)
N4—H4⋯N3^i	0.95 (3)	2.18 (4)	2.887 (4)	131 (2)

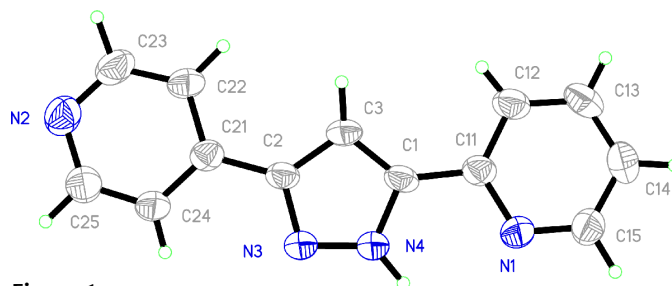Symmetry code: (i) $1 - x, 1 - y, 1 - z$.

Figure 1
The molecular structure of (I), showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 50% probability level.
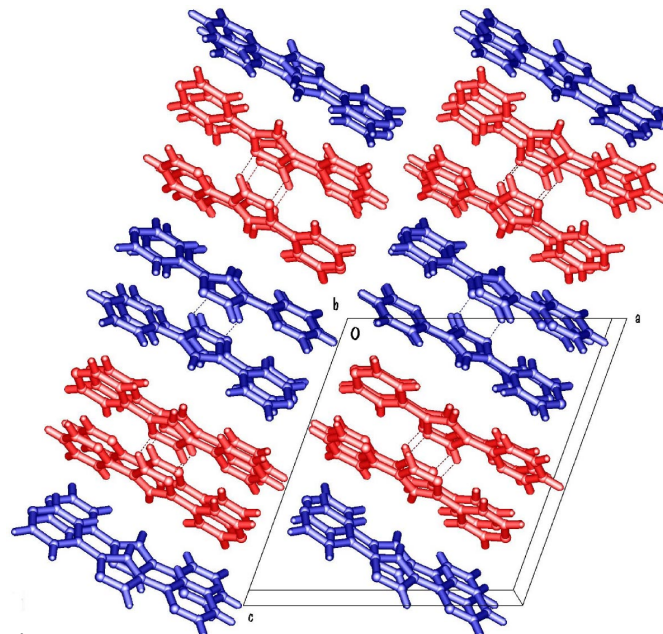

Figure 2
The crystal structure of (I), showing the packing mode of the dimers.

All H atoms were located in ΔF syntheses and refined with isotropic displacement parameters.

Data collection: *Enraf–Nonius CAD-4 Diffractometer Program* (Schagen *et al.*, 1988); cell refinement: *Enraf–Nonius CAD-4 Diffractometer Program*; data reduction: *XCAD4* (Harms, 1997); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *OLEX* (Dolomanov *et al.*, 2003); software used to prepare material for publication: *SHELXL97*..

References

Catalano, V. J. & Craig, T. J. (2003). *Inorg. Chem.* **42**, 321–324.
Dolomanov, O. V., Blake, A. J., Champness, N. R. & Schröder, M. (2003). *J. Appl. Cryst.* **36**, 1283–1284.
Ferles, M., Liboska, R. & Trska, P. (1990). *Collect. Czech. Chem. Commun.* **55**, 1228–1232.
Harms, K. (1997). *XCAD4*. University of Marburg, Germany.

Khlobystov, A. N., Blake, A. J., Champness, N. R., Lemenovskii, D. A., Majouga, A. G., Zyk, N. V. & Schröder, M. (2001). *Coord. Chem. Rev.* **222**, 155–192.

Pons, J., Chadghan, A., Casabo, J., Alvares-Larena, A., Piniella, J. F. & Ros, J. (2001). *Polyhedron*, **20**, 2531–2536.

Schagen, J. D., Strauer, L., van Meurs, F. & Williams, G. (1988). *Enraf–Nonius CAD*-4 *Diffractometer Program*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.

Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.