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3,4,6-Tris(pyrazol-1-yl)pyridazine

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Key indicators

Single-crystal X-ray study
T = 298 K
Mean σ(C–C) = 0.010 Å
R factor = 0.081
wR factor = 0.168
Data-to-parameter ratio = 8.9

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

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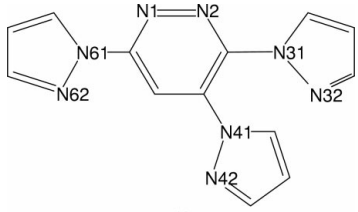
In the structure of the title compound, $C_{13}H_{10}N_8$, a tetradentate N_4-donor ligand derivatized on the pyridazine backbone with a monodentate N-donor group, the four potentially coordinating N atoms of the pyridazine and 3- and 6-pyrazole rings adopt a *trans–trans* conformation. Although the 6-substituted pyrazole ring is almost coplanar with the pyridazine ring, the 3- and 4-substituted pyrazole rings are severely bent out of the plane of the pyridazine ring. These features suggest that it may not be possible to arrange the four adjacent N-donors such that the molecule can act as a bis-bidentate chelating ligand. An analysis of the extended structure of the title compound reveals a very short, offset face-to-face π–π interaction involving the pyridazine and 6-substituted pyrazole rings of adjacent molecules.

Comment

Pyridazines substituted in the 3- and 6-positions with N-donor ligands act as tetradentate N_4-donor ligands in a bis-bidentate chelating fashion, generating multinuclear coordination complexes with relatively short internuclear separations [$d(M\cdots M)$ *ca* 3.6 Å; Thompson *et al.*, 1985; Youinou *et al.*, 1992, Hubberstey & Russell, 1995].



(I)

In an attempt to introduce a third ligating centre to these molecules, we have prepared 3,4,6-tris(pyrazol-1-yl)-pyridazine, (I), a bis-bidentate N_4-donor ligand derivatized on the pyridazine backbone with a monodentate N-donor group. Its molecular structure is shown in Fig. 1. Two noteworthy points emerge. Firstly, the four potentially coordinating N atoms of the pyridazine and 3- and 6-pyrazole rings (N1, N2, N32 and N62) adopt a *trans–trans* conformation, which contrasts with the *cis–cis* conformation required for the tetradentate N_4-donor ligands to act in a bis-bidentate chelating fashion. Secondly, although the 6-substituted pyrazole ring is almost coplanar with the pyridazine ring [dihedral angle 5.5 (4)°], the 3- and 4-substituted pyrazole rings are severely bent out of the plane of the pyridazine ring [dihedral angles 40.2 (3) and 51.2 (2)°, respectively]. Unfortunately, both points, but especially the latter, which can be attributed to steric conflict between the adjacent pyrazole substituents on the 3- and 4-positions of the pyridazine ring, suggest that it

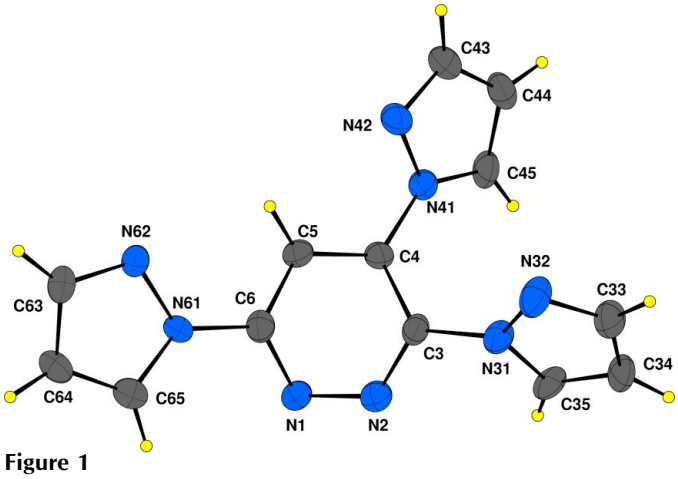


Figure 1
The molecular structure and atom-numbering scheme of 3,4,6-tris(pyrazol-1-yl)pyridazine. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as spheres of arbitrary radii.

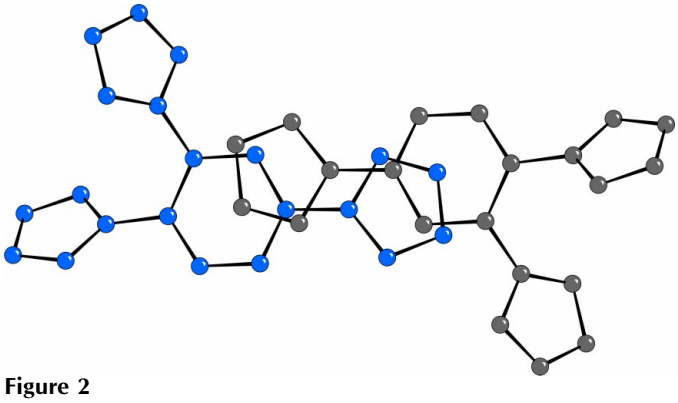


Figure 2
A projection of the structure of two molecules onto the least-squares mean plane containing the pyridazine and 6-substituted pyrazole rings of one molecule, showing the π–π-stacking interactions between adjacent molecules.

may not be possible to arrange the four adjacent N-donor centres for it to act as a bis-bidentate chelating ligand.

An analysis of the extended structure reveals the existence of a very short, offset face-to-face π–π interaction involving the pyridazine and 6-substituted pyrazole ring of adjacent molecules (Fig. 2). The perpendicular separation between the least-squares mean planes through these two rings [the maximum deviation of fitted atoms from best plane is 0.10 Å] is very short [3.339 (12) Å; range 3.244–3.409 Å]. As each tris(pyrazol-1-yl)pyridazine molecule forms part of a weakly C—H···N hydrogen-bonded chain [C34—H34 = 0.93, H34···N42 = 2.62, C34···N42 = 3.515 (8) Å and C34—H34···N42 = 162°; C35—H35 = 0.93, H35···N62 = 2.50, C35···N62 = 3.413 (8) Å and C35—H36···N62 = 168°] aligned in the [101] direction (Fig. 3), the offset π–π interactions link the chains to give a three-dimensional matrix (Fig. 4).

Experimental

Sodium hydride (0.98 g, 245 mmol) was added to a solution of pyrazole (1.12 g, 165 mmol) in pre-dried tetrahydrofuran (50 ml). After stirring the mixture for 20 min, 3,4,6-trichloropyridazine

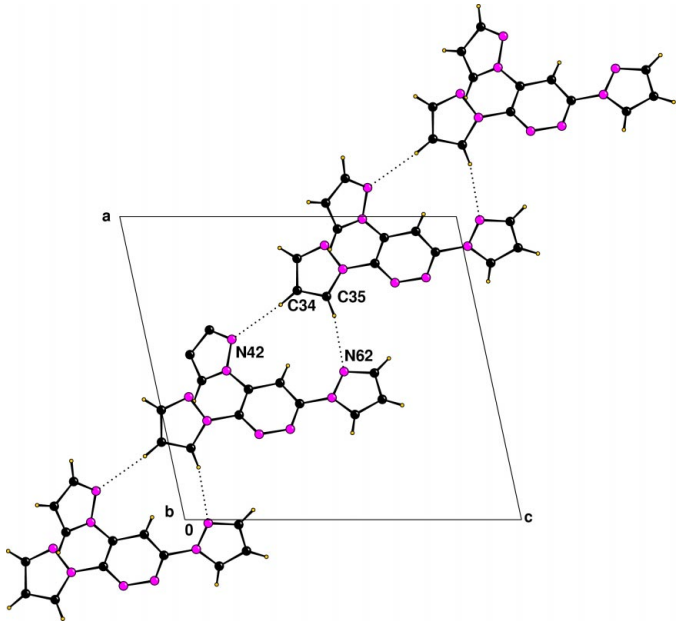


Figure 3
A projection of the structure on to the (010) plane, showing the C34—H34···N62 and C35—H35···N42 hydrogen-bonding interactions, which generate the chain of molecules aligned along the [101] direction. Key: C black circles, N blue circles and H small yellow circles.

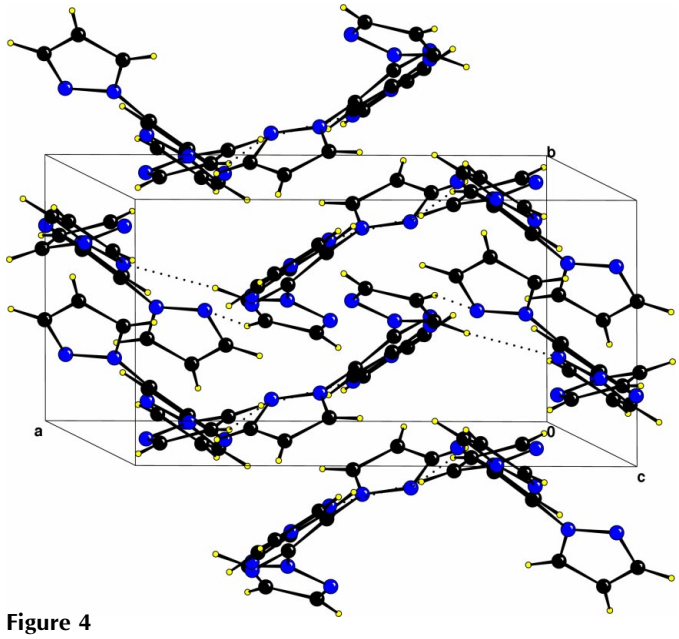


Figure 4
A view of the structure showing the π–π-stacking interactions linking the hydrogen-bonded chains. Key: C black circles, N blue circles and H small yellow circles.

(1.00 g, 54 mmol) was added to the solution (CAUTION: exothermic reaction!) and the mixture stirred for a further 60 min. After cooling to room temperature, the solvent was removed and the resultant solid dissolved in dichloromethane (40 ml) and washed with water (3 × 30 ml). The organic layer was dried over magnesium sulfate and the solvent removed to give a white powder, which was recrystallized from ethanol (yield; 1.32 g, 47 mmol, 88%) to give crystals suitable for diffraction analysis. Found (calculated for $C_{13}H_{10}N_8$): C 55.90 (56.10), H 3.60 (3.60), N 40.20% (40.25%). IR (KBr disc) (ν/cm^{-1}):

3132 (*m*), 1594 (*s*), 1562 (*s*), 1526 (*s*), 1456 (*s*), 1424 (*s*), 1396 (*s*), 1336 (*s*), 1323 (*m*), 1198 (*s*), 1189 (*m*), 1175 (*s*), 1113 (*m*), 1098 (*m*), 1059 (*s*), 1045 (*s*), 1031 (*s*), 1015 (*s*), 954 (*s*), 939 (*s*), 902 (*s*), 893 (*s*), 865 (*m*), 811 (*s*), 777 (*s*), 759 (*s*), 669 (*m*), 649 (*m*), 624 (*s*), 599 (*s*), 584 (*m*), 521 (*m*), 487 (*m*), 443 (*m*). ^{1}H NMR ($CDCl_3$) δ/p.p.m.: 6.45 (*m*, 1H), 6.68 (*m*, 2H), 6.80 (*d*, 1H), 7.81 (*d*, 1H), 7.84 (*d*, 1H), 7.93 (*d*, 1H), 8.21 (*dd*, 1H), 8.71 (*s*, 1H), 8.84 (*dd*, 1H). EI–MS (*m*/*z*) 278 $[C_{13}H_{10}N_8]^+$.

Crystal data

$C_{13}H_{10}N_8$	D_x = 1.429 Mg m^{-3}
M_r = 278.29	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 29 reflections
a = 13.190 (5) Å	θ = 10.0–12.0°
b = 7.003 (3) Å	μ = 0.10 mm^{-1}
c = 14.326 (4) Å	T = 298 (2) K
β = 102.14 (3)°	Plate, colourless
V = 1293.7 (8) Å^3	0.23 × 0.23 × 0.02 mm
Z = 4	

Data collection

Stoe Stadi-4 four-circle diffractometer	θ_{max} = 22.5°
ω/θ scans	$h = -14 \rightarrow 14$
Absorption correction: none	$k = 0 \rightarrow 7$
3374 measured reflections	$l = -15 \rightarrow 15$
1688 independent reflections	3 standard reflections
856 reflections with $I > 2\sigma(I)$	frequency: 60 min
R_{int} = 0.117	intensity decay: none

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.014P)^2 + 1.704P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)]$ = 0.081	$(\Delta/\sigma)_{max}$ = 0.001
$wR(F^2)$ = 0.168	$\Delta\rho_{max}$ = 0.19 e Å^{-3}
S = 1.19	$\Delta\rho_{min}$ = −0.27 e Å^{-3}
1688 reflections	
190 parameters	
H-atom parameters constrained	

This crystal diffracted only to low resolution. No significant diffraction occurred beyond 2θ of 45°, which accounts for the high value of R_{int} (0.117). All H atoms were included at geometrically calculated positions and constrained to ride at a distance of 0.93 Å from their parent C atoms, with $U_{iso}(H) = 1.2U_{eq}(C)$.

Data collection: *STADI*4 (Stoe & Cie, 1997); cell refinement: *STADI*4; data reduction: *X-RED* (Stoe & Cie, 1997); program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *CAMERON* (Watkin *et al.*, 1996); software used to prepare material for publication: *SHELXL*97 and *PLATON* (Spek, 2002).

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