Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

3,6-Di(thiophen-2-yl)pyridazine

Brian Ackers, Alexander J. Blake,* Stuart J. Hill and Peter Hubberstey

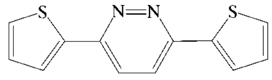
School of Chemistry, The University of Nottingham, University Park, Nottingham NG7 2RD, England
Correspondence e-mail: a.j.blake@nottingham.ac.uk

Received 27 August 2002
Accepted 4 September 2002
Online 11 October 2002

Molecules of the title compound, $C_{12}H_8N_2S_2$, which are effectively planar, have all four heteroatoms on the same side but do not have twofold symmetry.

Comment

3,6-Disubstituted pyridazines can act as bis-bidentate chelating ligands to generate dinuclear complexes with $M\cdots M$ distances of approximately 3.6 Å. Many dicopper systems have been prepared with N_4-donor ligands containing 2-aminopyridine or 1-pyrazole as substituents (Hubberstey & Russell, 1995; Thompson *et al.*, 1985). To extend and diversify this chemistry, we have synthesized a number of N_2S_2-donor ligands, including 3,6-bis(thiophen-2-yl)pyridazine, (I). This molecule, first prepared by the cross-coupling of 3,6-dichloropyridazine with the Grignard reagent obtained by treatment of 2-bromothiophene with Mg (Montheard & Dubois, 1985), and subsequently by thermal decomposition of either 2,7-dihydro-1,4,5-thiadiazepine, obtained by condensation of 1,5-di(thiophen-2-yl)-3-thiapentane-1,5-dione with hydrazine (Nakayama *et al.*, 1989), or 4,5-dihydropyridazine, obtained by condensation of 1,4-di(thiophen-2-yl)-1,4-dione with hydrazine (Kossmehl *et al.*, 1993), has been little studied. Our attempts to prepare coordination complexes of (I) with Cu^{II}, Cu^{I} and Pd^{II} have been unsuccessful.



(I)

Although the two thiophene rings of (I) are crystallographically independent (Fig. 1), their conformation is such that all four heteroatoms are located on the same side of the molecule. The adopted conformation is such that the molecules do not possess twofold symmetry, but do have approximate non-crystallographic C_s symmetry. This arrangement differs from that in previously structurally characterized disubstituted pyridazines, where the heteroatoms of the substituent rings are *trans* with respect to the N atoms of the pyridazine ring (Blake *et al.*, 2002). An explanation is not immediately obvious in view of, first, the steric interactions between atoms H4 and H35 (2.40 Å), and between H5 and H65 (2.36 Å), which result in the three aromatic rings not being coplanar [the dihedral angles between the central and terminal rings are 11.18 (14)° (pyridazine N1/N2/C3–C6 and thiophene C31/S32/C33–C35) and 14.91 (14)° (pyridazine N1/N2/C3–C6 and thiophene C61/S62/C63–C65), and that between the terminal rings is 7.9 (2)°], and, secondly, the absence of the hydrogen-bonding interactions (C35—H35$\cdots$N2 and C65—H65$\cdots$N1), however weak, that would result from the alternative conformation.

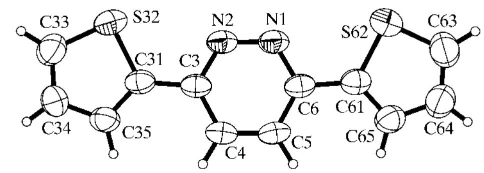


Figure 1
A view of (I) with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

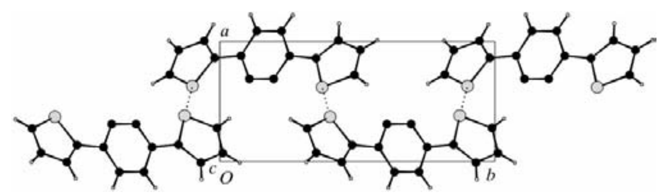


Figure 2
A projection of the structure of (I) on to the (001) plane, showing the weak intermolecular S$\cdots$S contacts and the resulting chain architecture. S atoms are denoted by large pale-grey circles, C atoms by intermediate black circles, N atoms by intermediate dark-grey circles and H atoms by small pale-grey circles.

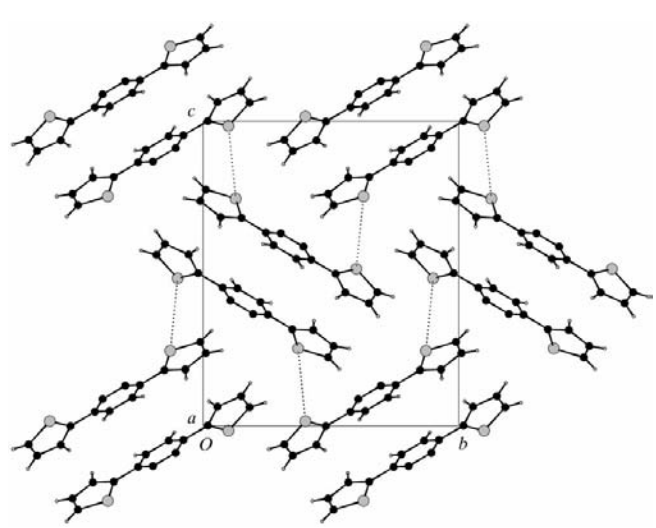


Figure 3
A projection of the structure of (I) on to the (100) plane, showing the interdigitation of the chain architecture. The shading scheme is the same as that in Fig. 2.

  DOI: 10.1107/S0108270102016037

An analysis of the extended structure of (I) reveals the only intermolecular forces present to be weak S···S contacts [S32···S62[i] 3.980 (2) Å; symmetry code: (i) $1-x, \frac{1}{2}+y, \frac{1}{2}-z$]. As a result of these interactions, the molecules of (I) form chains which lie along the *b* axis (Fig. 2) and which interdigitate to form a planar arrangement parallel to the (100) plane (Fig. 3).

Although there is the potential for a C33—H33···N1[i] hydrogen bond with an acceptable C—H···N angle of 160°, the long C33···N1[i] and H33···N1 distances of 3.503 (3) and 2.62 Å, respectively, and the unfavourable H···N—N and H···N—C angles of 91 and 141°, indicate that this is, at most, a rather weak interaction.

Experimental

2-Bromothiophene (6.33 ml, 10.76 g, 33 mmol) in pre-dried diethyl ether (30 ml) was added slowly to dry Mg turnings (1.60 g, 66 mmol) in pre-dried diethyl ether (20 ml) and the resulting mixture stirred until the Mg dissolved completely. After cooling to 273 K, dichloro[bis(diphenylphosphino)propane]nickel(II) (0.067 g, 0.12 mmol) and 3,6-dichloropyridazine (5.0 g, 33 mmol) in pre-dried diethyl ether (30 ml) were added consecutively. After stirring for 48 h, the solid product was filtered off, washed with HCl (2 *M*, 50 ml), dissolved in hot acetone (250 ml), filtered, and precipitated by addition of water. Recrystallization from an acetone–water (1:1) mixture gave tiny golden needles of (I) (1.6 g, 0.70 mmol, 20% yield). Analysis found (calculated for $C_{12}H_8N_2S_2$): C 58.85 (59.00), H 3.20 (3.25), N 11.50% (11.45%); m.p. 447–449 K (literature value: 448–449 K; Montheard & Dubois, 1985). Larger yellow tabular crystals of (I), used for the X-ray analysis, were recovered from a failed attempt to prepare a dinuclear palladium(II) chloride complex, in which (I) was expected to act as a bis-bidentate ligand bridging two Pd^{II} centres.

Crystal data

$C_{12}H_8N_2S_2$	Mo $K\alpha$ radiation
$M_r = 244.32$	Cell parameters from 29 reflections
Orthorhombic, $P2_12_12_1$	$\theta = 26.3–35.0°$
$a = 5.6862$ (4) Å	$\mu = 0.43$ mm^{-1}
$b = 13.0264$ (8) Å	$T = 298$ (2) K
$c = 15.563$ (2) Å	Tablet, yellow
$V = 1152.76$ (18) Å^3	0.68 × 0.51 × 0.39 mm
$Z = 4$	
$D_x = 1.408$ Mg m^{-3}	

Data collection

Stoe Stadi-4 four-circle diffractometer	$\theta_{max} = 25°$
ω/θ scans	$h = -6 \rightarrow 6$
3064 measured reflections	$k = -15 \rightarrow 15$
2031 independent reflections	$l = 0 \rightarrow 18$
1878 reflections with $I > 2\sigma(I)$	3 standard reflections
$R_{int} = 0.012$	frequency: 60 min
	intensity decay: 6%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.025P)^2 + 0.351P]$
$R[F^2 > 2\sigma(F^2)] = 0.032$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.074$	$(\Delta/\sigma)_{max} < 0.001$
$S = 1.11$	$\Delta\rho_{max} = 0.16$ e Å^{-3}
2031 reflections	$\Delta\rho_{min} = -0.21$ e Å^{-3}
145 parameters	Absolute structure: Flack (1983)
H-atom parameters constrained	Flack parameter = 0.01 (10)

A total of 822 Friedel pairs was employed in the estimation of the Flack (1983) parameter. Aromatic H atoms, after location from difference Fourier syntheses, were placed geometrically and refined with a riding model, with C—H = 0.93 Å and $U_{iso}(H) = 1.2U_{eq}(C)$.

Data collection: *STADI*4 (Stoe & Cie, 1995); cell refinement: *STADI*4; data reduction: *X-RED* (Stoe & Cie, 1995); program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1998) and *CAMERON* (Watkin *et al.*, 1996); software used to prepare material for publication: *SHELXL*97 and *PLATON* (Spek, 2002).

We thank the EPSRC (UK) for the provision of a diffractometer and for financial support to BA and SJH.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG1137). Services for accessing these data are described at the back of the journal.

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