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A new polymorph of 2,5-bis(4-pyridyl)-1,3,4-thiadiazole

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Key indicators

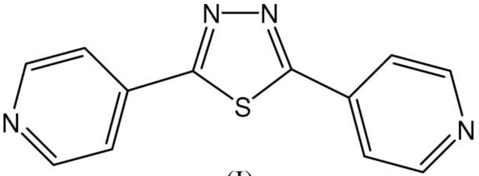
Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.003 Å
R factor = 0.032
wR factor = 0.101
Data-to-parameter ratio = 12.0

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

A new polymorph of 2,5-bis(4-pyridyl)-1,3,4-thiadiazole, $C_{12}H_8N_4S$, obtained under hydrothermal conditions, is described. In this structure, the two terminal pyridyl groups are inclined to the central thiadiazole ring with dihedral angles of 6.47 (2) and 29.95 (5)°, and the dihedral angle between the pyridyl ring planes is 23.65 (6)°. An intermolecular C—H···N weak interaction is observed. The structural differences of two polymorphs of 2,5-bis(4-pyridyl)-1,3,4-thiadiazole are also discussed.

Comment

Recently, we have reported the crystal structure of 2,5-bis(4-pyridyl)-1,3,4-thiadiazole [form A, monoclinic, $C2/c$, with lattice parameters of a = 26.179 (9) Å, b = 5.8223 (17) Å, c = 7.169 (3) Å and β = 105.855 (9)°], which is obtained by recrystallizing the commercial product from a hot CH_3OH/H_2O solution (Du *et al.*, 2004). During our efforts to investigate the assembly of metal-organic coordination frameworks based on this bent dipyridyl linker, a new polymorph (form B), (I), was generated accidentally under hydrothermal conditions; the crystal structure of (I) is described in this paper.



(I)

The molecular structure of (I), shown in Fig. 1, contains no crystallographically imposed symmetry; however, a crystallographic twofold axis was detected in the structure of polymorph A. The two pyridyl rings make dihedral angles of 6.47 (2) and 29.95 (5)° with the central thiadiazole system, and the dihedral angle between them is 23.65 (6)°. The corresponding values in polymorph A are 21.8 (2), 21.8 (2) and

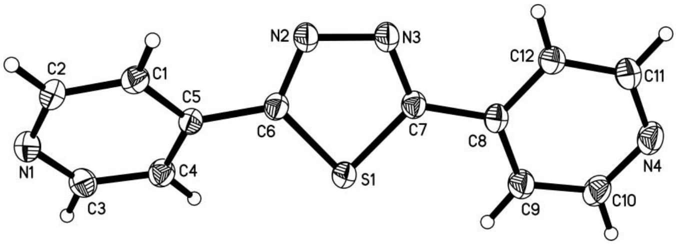


Figure 1
A view of the molecular structure of (I), with the atom-labeling scheme and 30% probability displacement ellipsoids.

43.0 (2)°, respectively. Selected bond lengths and angles are listed in Table 1. For the pyridyl rings, the C—N bond lengths (mean value 1.329 Å), are within the range of values normally considered standard for single C—N (1.47 Å) and double C═N (1.28 Å) bonds. The C—N bond lengths in the thiadiazole ring are 1.302 (2) and 1.298 (2) Å. All these bond geometries are comparable to those in polymorph *A*. Additionally, the angle between the center of the thiadiazole ring and the two pyridyl N-atom donors is 161°, and the separation of these two N atoms is 10.785 (2) Å. The corresponding parameters in polymorph *A* are 156° and 10.763 (4) Å.

No significant interactions, such as hydrogen bonds or π–π stacking, are observed in polymorph *A*. Notably, analysis of the crystal packing of this structure (polymorph *B*) suggests weak C2—H2···N4 intermolecular interactions, resulting in a one-dimensional chain along the [100] direction (Fig. 2). The relevant hydrogen-bonding parameters are listed in Table 2. Additionally, the interplanar distance between two layers of molecules is 3.5–3.8 Å, and the centroid-to-centroid distance is about 3.743 Å, indicating the existence of aromatic stacking interactions. Examination of this structure with *PLATON* (Spek, 2003) reveals no solvent-accessible voids in the unit cell.

Experimental

A mixture of $Zn(OAc)_2\cdot 4H_2O$ (21.8 mg, 0.1 mmol), isophthalic acid (16.8 mg, 0.10 mmol), and 2,5-bis(4-pyridyl)-1,3,4-thiadiazole (23.5 mg, 0.1 mmol) in water (10 ml) was heated at 433 K for 3 d in a sealed Teflon-lined stainless steel vessel (20 ml) under autogenous pressure. After the reaction mixture was slowly cooled to room temperature at a rate of 5 K h^{-1}, pale-yellow lamellar single crystals suitable for X-ray diffraction were produced.

Crystal data

$C_{12}H_8N_4S$
M_r = 240.28
Monoclinic, $P2_1/c$
a = 13.395 (2) Å
b = 7.1833 (11) Å
c = 11.4151 (18) Å
β = 104.948 (2)°
V = 1061.2 (3) Å^3
Z = 4

D_x = 1.504 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 1940 reflections
θ = 3.2–27.3°
μ = 0.28 mm^{-1}
T = 293 (2) K
Plate, pale yellow
0.30 × 0.24 × 0.08 mm

Data collection

Bruker APEX-II CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.770, T_{max} = 1.000
5414 measured reflections

1862 independent reflections
1515 reflections with $I > 2\sigma(I)$
R_{int} = 0.023
θ_{max} = 25.0°
$h = -15 \rightarrow 15$
$k = -8 \rightarrow 4$
$l = -13 \rightarrow 13$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.032
$wR(F^2)$ = 0.102
S = 1.07
1862 reflections
155 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0679P)^2 + 0.0172P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.23 e Å^{-3}
$\Delta\rho_{min}$ = −0.22 e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.009 (2)

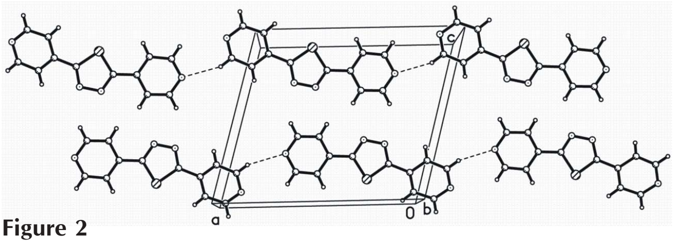


Figure 2
Crystal packing of (I), showing the one-dimensional chain along the [100] direction. Dashed lines indicate weak C2—H2···N4 intermolecular interactions.

Table 1
Selected geometric parameters (Å, °).

S1—C6	1.7141 (17)	N2—N3	1.365 (2)
S1—C7	1.7182 (18)	N3—C7	1.298 (2)
N1—C3	1.325 (2)	N4—C11	1.325 (3)
N1—C2	1.337 (2)	N4—C10	1.330 (3)
N2—C6	1.302 (2)		
C6—S1—C7	86.79 (8)	C4—C5—C1	117.60 (16)
C3—N1—C2	116.62 (16)	N2—C6—S1	114.29 (14)
C6—N2—N3	112.18 (15)	N3—C7—S1	113.96 (13)
C7—N3—N2	112.76 (15)	C9—C8—C12	117.51 (16)
C11—N4—C10	116.29 (16)	C8—C9—C10	118.96 (18)
C2—C1—C5	119.13 (16)	N4—C10—C9	124.13 (18)
N1—C2—C1	123.72 (17)	N4—C11—C12	124.33 (17)
N1—C3—C4	124.03 (17)	C11—C12—C8	118.76 (17)
C3—C4—C5	118.91 (16)		

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C2—H2···N4^{i}	0.93	2.57	3.361 (3)	143

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

Although all H atoms were visible in difference Fourier maps, they were placed in geometrically calculated positions with C—H = 0.93 Å and included in the final refinement in the riding-model approximation, with displacement parameters derived from their parent atoms [U_{iso}(H) = 1.2U_{eq}(C)].

Data collection: *APEX-II* (Bruker, 2003); cell refinement: *APEX-II*; data reduction: *SAINT* (Bruker, 2001); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2001); software used to prepare material for publication: *SHELXTL*.

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