

2,3,5,6-Tetrakis[(pyridin-2-yl)sulfanyl]methylpyrazine

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Received 10 December 2016

Accepted 10 December 2016

Edited by W. T. A. Harrison, University of Aberdeen, Scotland

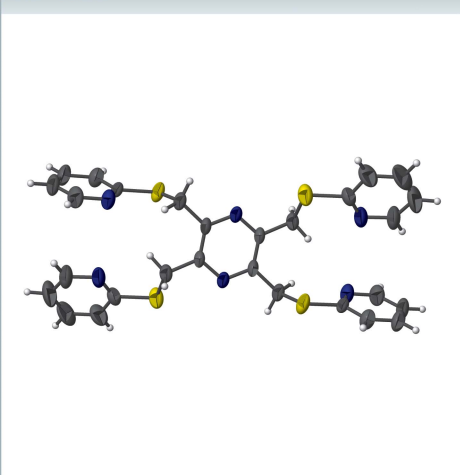
Keywords: crystal structure; tetrakis-substituted; pyrazine; pyridin-2-ylsulfanyl derivative; inversion symmetry; C—H... π interactions; offset π — π interactions.

CCDC reference: 1521950

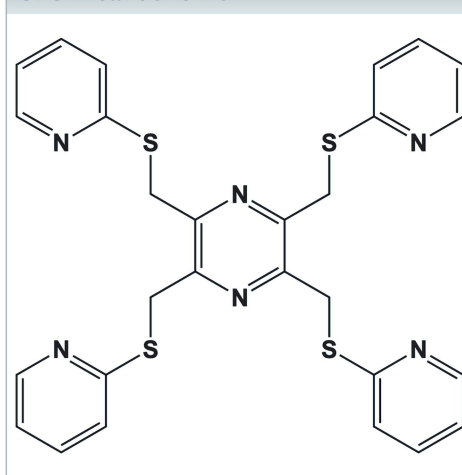
Structural data: full structural data are available from iucrdata.iucr.org

The title compound, C₂₈H₂₄N₆S₄, synthesized by the reaction of 2,3,5,6-tetrakis(bromomethyl)pyrazine with 2-mercaptopyridine, crystallizes with one half-molecule in the asymmetric unit. The whole molecule is generated by inversion symmetry, the centre of the pyrazine ring being located about an inversion centre. The pyridine rings of the unique (pyridin-2-ylsulfanyl)methyl substituents are inclined to the pyrazine ring by 38.7 (3) and 75.6 (2)°, and by 66.0 (3)° to one another. In the crystal, molecules are linked *via* C—H... π interactions, forming chains along the *b*-axis direction. The chains are linked by offset π — π interactions [intercentroid distance = 3.682 (3) Å], forming layers lying parallel to the *bc* plane.

3D view



Chemical scheme



Structure description

The title compound is one of a series of tetra-substituted pyrazine compounds (Pacífico & Stoeckli-Evans, 2004; Assoumatine *et al.*, 2007; Assoumatine & Stoeckli-Evans, 2014*a*), prepared in order to study their coordination behaviour with various transition metals (Assoumatine, 1999). It was synthesized by the reaction of 2,3,5,6-tetrakis(bromomethyl)pyrazine (Assoumatine & Stoeckli-Evans, 2014*b*), with 2-mercaptopyridine. The synthesis and crystal structure of 2,3,5,6-tetrakis(bromomethyl)pyrazine have been reported (Assoumatine & Stoeckli-Evans, 2014*b*).

The title compound, crystallizes with one half-molecule in the asymmetric unit (Fig. 1). The whole molecule is generated by inversion symmetry, the centre of the pyrazine ring being located about an inversion centre. The pyridine rings (N2/C4—C8 and N3/C10—C14) of the unique (pyridin-2-ylsulfanyl)methyl substituents are inclined to the pyrazine ring by 38.7 (3) and 75.6 (2)°, respectively, and by 66.0 (3)° to one another. In the phenyl analogue of the title compound, *viz.* 2,3,5,6-tetrakis[(phenylsulfanyl)methyl]pyrazine

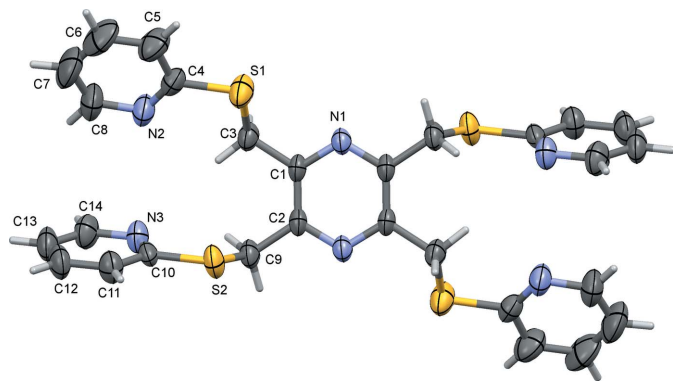


Figure 1
A view of the molecular structure of the title compound, showing the atom labelling. Displacement ellipsoids are drawn at the 50% probability level. Unlabelled atoms are related to labelled atoms by the symmetry operation $(-x, 1 - y, 1 - z)$.

(Assoumatine *et al.*, 2007), the corresponding dihedral angles are 19.15 (7), 79.58 (7) and 60.45 (8) $^\circ$, respectively.

In the crystal, molecules are linked *via* C–H $\cdots\pi$ interactions, forming chains along [010]; see Table 1 and Fig. 2. The chains are linked by offset π – π interactions, forming layers lying parallel to the *bc* plane, as shown in Fig. 3. The inter-centroid distances are $Cg1\cdots Cg3^i = Cg1\cdots Cg3^{ii} = 3.682$ (3) Å, interplanar distances = 3.554 (2) Å, offsets = 1.142 Å; *Cg1* and *Cg3* are the centroids of the pyrazine ring and the pyridine ring N3/C10–C14; symmetry codes: (i) $-x + 2, y + \frac{1}{2}, -z + \frac{3}{2}$; (ii) $x, -y + \frac{1}{2}, z + \frac{1}{2}$. There are no other significant intermolecular interactions present in the crystal.

Synthesis and crystallization

To a magnetically stirred solution of 2-mercaptopyridine (4 g, 35.4 mmol; Aldrich, 99%) in CH_2Cl_2 (100 ml), were added 2,3,5,6-tetrakis(bromomethyl)pyrazine (4 g, 8.85 mmol) and triethylamine (5 ml, 35.4 mmol; Fluka, 99.5%). The contents

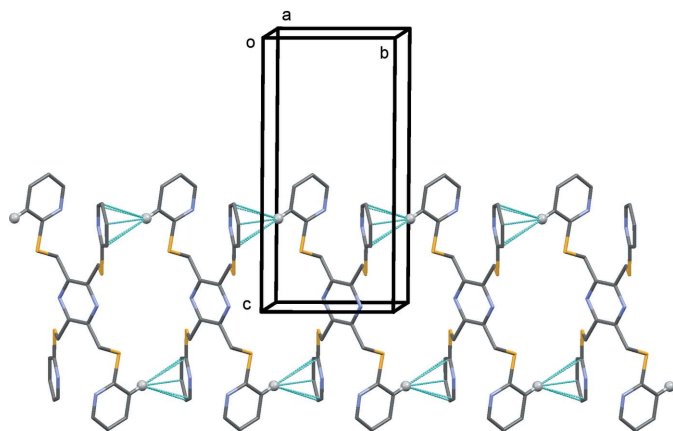


Figure 2
A partial view along the *a* axis of the crystal packing of the title compound. The C–H $\cdots\pi$ interactions are represented by dashed lines (Table 1), and, for clarity, only H atom H11 (grey ball) has been included.

Table 1
Hydrogen-bond geometry (Å, $^\circ$).

Cg2 is the centroid of pyridine ring N2/C4–C8.

<i>D</i> –H \cdots <i>A</i>	<i>D</i> –H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> –H \cdots <i>A</i>
C11–H11 \cdots Cg2 ⁱ	0.93	2.93	3.804 (6)	156

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

were heated at reflux for 30 min, cooled to room temperature, and diluted with CH_2Cl_2 (100 ml). The organic solution was washed with water (3 \times 30 ml) and a saturated solution of NaCl (1 \times 30 ml), dried over anhydrous $MgSO_4$ and evaporated to dryness on a rotary evaporator after filtration. The resultant yellowish residue was recrystallized from acetonitrile solution and dried under vacuum to afford the title compound (yield 4.56 g, 90%; m.p. 422–423 K). R_f 0.48 (solvent CH_2Cl_2 , eluent $CHCl_3/MeCO_2Et$, 7/5 *v/v*). Pale-yellow blocks were prepared by diffusion of an equal volume of ethanol into a concentrated $CHCl_3$ (4 ml) solution of the title compound. Spectroscopic and analytical data: The principal peaks of the IR spectrum (KBr disc, cm^{-1}) are: $\nu = 1579$ vs, 1556 s, 1453 s, 1414 vs, 1124 vs, 754 vs, 723 s. 1H RMN ($CDCl_3$, 400 MHz): $\delta = 8.35$ [ddd, $^3J(6,5) = 4.9, ^4J(6,4) = 1.8, ^5J(6,3) = 0.9$, 4H, 6-PyH], 7.44 [ddd, $^3J(4,3) = 8.1, ^3J(4,5) = 7.4, ^4J(4,6) = 1.9$, 4H, 4-PyH], 7.24 [ddd, $^3J(3,4) = 8.1, ^4J(3,5) = ^5J(3,6) = 1.0$, 4H, 3-PyH], 6.95 [ddd, $^3J(5,4) = 7.3, ^3J(5,6) = 4.9, ^4J(5,3) = 1.0$, 4H, 5-PyH], 4.80 (s, 8H, Pz–CH₂–S) p.p.m. ^{13}C RMN ($CDCl_3$, 100 MHz): $\delta = 159.01, 150.23, 149.88, 136.74, 122.65, 120.27, 33.88$ p.p.m. Analysis for $C_{28}H_{24}N_6S_4$ ($M_r = 572.82$ g mol $^{-1}$); calculated:

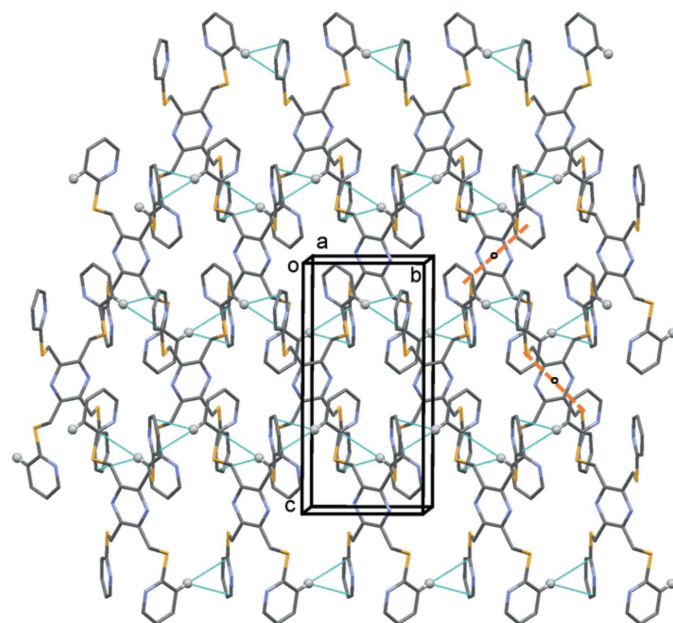


Figure 3
A view along the *a* axis of the crystal packing of the title compound. The C–H $\cdots\pi$ interactions (Table 1) are represented by cyan dashed lines, and examples of the π – π interactions by orange dashed lines. For clarity, only H atom H11 (grey ball) has been included.

Table 2

Experimental details.

Crystal data	
Chemical formula	C ₂₈ H ₂₄ N ₆ S ₄
<i>M_r</i>	572.77
Crystal system, space group	Monoclinic, <i>P</i> 2 ₁ / <i>c</i>
Temperature (K)	293
<i>a</i> , <i>b</i> , <i>c</i> (Å)	11.8139 (12), 7.4803 (11), 15.5204 (10)
β (°)	96.766 (8)
<i>V</i> (Å ³)	1362.0 (3)
<i>Z</i>	2
Radiation type	Mo <i>K</i> α
μ (mm ⁻¹)	0.38
Crystal size (mm)	0.27 × 0.25 × 0.15
Data collection	
Diffractometer	Stoe AED2 four-circle
No. of measured, independent and observed [<i>I</i> > 2 σ (<i>I</i>)] reflections	3360, 2523, 1590
<i>R</i> _{int}	0.035
(sin θ / λ) _{max} (Å ⁻¹)	0.606
Refinement	
<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.069, 0.130, 1.14
No. of reflections	2523
No. of parameters	173
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ (e Å ⁻³)	0.31, -0.24

Computer programs: *STADIA* and *X-RED* (Stoe & Cie, 1997), *SHELXS97* (Sheldrick, 2008), *Mercury* (Macrae *et al.*, 2008), *SHELXL2014* (Sheldrick, 2015), *PLATON* (Spek, 2009) and *publCIF* (Westrip, 2010).

C 58.71, H 4.23, N 14.68, S 22.39%; found: C 58.76, H 4.23, N 14.68, S 22.25%. MS (EI, 70 eV), *m/z* (%): 572 ([*M*⁺], 5.2).

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. No absorption correction was applied owing to the irregular shape of the crystal, and as there were no suitable reflections for ψ scans.

Acknowledgements

This work was supported by the Swiss National Science Foundation and the University of Neuchâtel.

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full crystallographic data

IUCrData (2016). **1**, x161977 [<https://doi.org/10.1107/S2414314616019775>]

2,3,5,6-Tetrakis{[(pyridin-2-yl)sulfanyl]methyl}pyrazine

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2,3,5,6-Tetrakis{[(pyridin-2-yl)sulfanyl]methyl}pyrazine

Crystal data

$C_{28}H_{24}N_6S_4$

$M_r = 572.77$

Monoclinic, $P2_1/c$

$a = 11.8139$ (12) Å

$b = 7.4803$ (11) Å

$c = 15.5204$ (10) Å

$\beta = 96.766$ (8)°

$V = 1362.0$ (3) Å³

$Z = 2$

$F(000) = 596$

$D_x = 1.397$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 28 reflections

$\theta = 14.0$ – 19.6 °

$\mu = 0.38$ mm⁻¹

$T = 293$ K

Block, pale yellow

$0.27 \times 0.25 \times 0.15$ mm

Data collection

Stoe AED2 four-circle

diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

$\omega/2\theta$ scans

3360 measured reflections

2523 independent reflections

1590 reflections with $I > 2\sigma(I)$

$R_{int} = 0.035$

$\theta_{max} = 25.5$ °, $\theta_{min} = 2.6$ °

$h = -14$ → 14

$k = 0$ → 9

$l = -18$ → 18

3 standard reflections every 120 min

intensity decay: 1%

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.069$

$wR(F^2) = 0.130$

$S = 1.14$

2523 reflections

173 parameters

0 restraints

Primary atom site location: structure-invariant

direct methods

Secondary atom site location: difference Fourier

map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0077P)^2 + 2.2742P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max} = 0.31$ e Å⁻³

$\Delta\rho_{min} = -0.24$ e Å⁻³

Extinction correction: SHELXL2014

(Sheldrick, 2015),

$Fc^* = kFc[1 + 0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$

Extinction coefficient: 0.0034 (4)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
S1	0.72006 (10)	0.7083 (2)	0.88691 (7)	0.0656 (5)
S2	0.87442 (11)	0.2016 (2)	0.80919 (7)	0.0579 (4)
N1	1.0653 (3)	0.3502 (5)	0.98745 (19)	0.0418 (9)
N2	0.6938 (3)	0.6825 (6)	0.7136 (2)	0.0646 (12)
N3	0.8849 (3)	0.3740 (6)	0.6582 (2)	0.0544 (11)
C1	0.9341 (3)	0.5756 (6)	0.9335 (2)	0.0372 (10)
C2	1.0000 (3)	0.4258 (6)	0.9210 (2)	0.0392 (11)
C3	0.8619 (3)	0.6669 (7)	0.8603 (2)	0.0473 (12)
H3A	0.8578	0.5926	0.8088	0.057*
H3B	0.8970	0.7794	0.8475	0.057*
C4	0.6412 (4)	0.7190 (7)	0.7825 (3)	0.0531 (13)
C5	0.5276 (4)	0.7658 (8)	0.7779 (4)	0.0784 (18)
H5	0.4942	0.7927	0.8277	0.094*
C6	0.4649 (5)	0.7715 (10)	0.6969 (5)	0.098 (2)
H6	0.3883	0.8033	0.6911	0.118*
C7	0.5171 (6)	0.7297 (10)	0.6251 (4)	0.104 (3)
H7	0.4760	0.7291	0.5702	0.125*
C8	0.6291 (5)	0.6895 (9)	0.6359 (3)	0.088 (2)
H8	0.6642	0.6651	0.5866	0.105*
C9	1.0016 (4)	0.3364 (7)	0.8342 (2)	0.0480 (12)
H9A	1.0687	0.2612	0.8354	0.058*
H9B	1.0052	0.4263	0.7896	0.058*
C10	0.8353 (4)	0.2440 (6)	0.6968 (2)	0.0441 (12)
C11	0.7524 (4)	0.1338 (7)	0.6552 (3)	0.0609 (14)
H11	0.7199	0.0431	0.6851	0.073*
C12	0.7194 (4)	0.1621 (8)	0.5681 (3)	0.0686 (16)
H12	0.6639	0.0902	0.5381	0.082*
C13	0.7684 (4)	0.2955 (8)	0.5268 (3)	0.0659 (15)
H13	0.7472	0.3164	0.4681	0.079*
C14	0.8497 (4)	0.3991 (8)	0.5729 (3)	0.0644 (15)
H14	0.8823	0.4914	0.5442	0.077*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0532 (7)	0.1041 (12)	0.0390 (6)	0.0141 (8)	0.0032 (5)	0.0054 (8)
S2	0.0748 (9)	0.0683 (9)	0.0284 (5)	-0.0127 (8)	-0.0025 (5)	-0.0026 (6)
N1	0.045 (2)	0.052 (2)	0.0272 (16)	0.0003 (18)	-0.0010 (14)	-0.0026 (17)
N2	0.063 (3)	0.087 (3)	0.040 (2)	0.011 (3)	-0.0095 (19)	0.001 (2)
N3	0.056 (2)	0.073 (3)	0.0325 (19)	-0.005 (2)	0.0009 (17)	0.001 (2)
C1	0.038 (2)	0.050 (3)	0.0222 (19)	-0.004 (2)	-0.0023 (16)	0.0036 (19)
C2	0.037 (2)	0.054 (3)	0.0246 (19)	-0.004 (2)	-0.0048 (17)	-0.001 (2)
C3	0.047 (3)	0.064 (3)	0.030 (2)	0.005 (2)	-0.0006 (18)	0.005 (2)
C4	0.048 (3)	0.057 (3)	0.050 (3)	0.004 (3)	-0.009 (2)	0.010 (3)
C5	0.051 (3)	0.100 (5)	0.082 (4)	0.017 (3)	-0.002 (3)	0.013 (4)

C6	0.054 (4)	0.111 (6)	0.121 (6)	0.013 (4)	-0.029 (4)	0.017 (5)
C7	0.084 (5)	0.133 (7)	0.083 (5)	0.011 (5)	-0.043 (4)	0.010 (5)
C8	0.090 (4)	0.115 (6)	0.049 (3)	0.013 (4)	-0.026 (3)	-0.005 (4)
C9	0.051 (3)	0.066 (3)	0.026 (2)	0.002 (2)	0.0009 (18)	-0.003 (2)
C10	0.046 (2)	0.057 (3)	0.028 (2)	0.008 (2)	-0.0018 (18)	-0.012 (2)
C11	0.068 (3)	0.067 (4)	0.045 (3)	-0.010 (3)	-0.004 (2)	-0.004 (3)
C12	0.068 (4)	0.089 (5)	0.044 (3)	-0.005 (3)	-0.014 (2)	-0.015 (3)
C13	0.065 (3)	0.098 (5)	0.032 (2)	0.006 (3)	-0.007 (2)	-0.005 (3)
C14	0.070 (3)	0.086 (4)	0.038 (2)	0.001 (3)	0.006 (2)	0.010 (3)

Geometric parameters (Å, °)

S1—C4	1.773 (4)	C5—C6	1.383 (7)
S1—C3	1.799 (4)	C5—H5	0.9300
S2—C10	1.780 (4)	C6—C7	1.371 (9)
S2—C9	1.813 (4)	C6—H6	0.9300
N1—C2	1.339 (5)	C7—C8	1.349 (8)
N1—C1 ⁱ	1.346 (5)	C7—H7	0.9300
N2—C4	1.328 (6)	C8—H8	0.9300
N2—C8	1.349 (5)	C9—H9A	0.9700
N3—C10	1.315 (6)	C9—H9B	0.9700
N3—C14	1.353 (5)	C10—C11	1.380 (6)
C1—N1 ⁱ	1.346 (5)	C11—C12	1.379 (6)
C1—C2	1.390 (6)	C11—H11	0.9300
C1—C3	1.502 (5)	C12—C13	1.353 (7)
C2—C9	1.506 (5)	C12—H12	0.9300
C3—H3A	0.9700	C13—C14	1.368 (7)
C3—H3B	0.9700	C13—H13	0.9300
C4—C5	1.380 (6)	C14—H14	0.9300
C4—S1—C3	101.7 (2)	C8—C7—H7	120.7
C10—S2—C9	102.9 (2)	C6—C7—H7	120.7
C2—N1—C1 ⁱ	117.9 (4)	N2—C8—C7	124.3 (6)
C4—N2—C8	116.3 (4)	N2—C8—H8	117.8
C10—N3—C14	116.5 (4)	C7—C8—H8	117.8
N1 ⁱ —C1—C2	121.1 (3)	C2—C9—S2	109.9 (3)
N1 ⁱ —C1—C3	116.3 (4)	C2—C9—H9A	109.7
C2—C1—C3	122.6 (3)	S2—C9—H9A	109.7
N1—C2—C1	120.9 (4)	C2—C9—H9B	109.7
N1—C2—C9	115.7 (4)	S2—C9—H9B	109.7
C1—C2—C9	123.3 (4)	H9A—C9—H9B	108.2
C1—C3—S1	111.5 (3)	N3—C10—C11	124.0 (4)
C1—C3—H3A	109.3	N3—C10—S2	120.0 (3)
S1—C3—H3A	109.3	C11—C10—S2	116.0 (4)
C1—C3—H3B	109.3	C12—C11—C10	118.0 (5)
S1—C3—H3B	109.3	C12—C11—H11	121.0
H3A—C3—H3B	108.0	C10—C11—H11	121.0
N2—C4—C5	123.7 (4)	C13—C12—C11	119.4 (5)

N2—C4—S1	118.8 (3)	C13—C12—H12	120.3
C5—C4—S1	117.5 (4)	C11—C12—H12	120.3
C4—C5—C6	117.9 (5)	C12—C13—C14	118.9 (4)
C4—C5—H5	121.1	C12—C13—H13	120.6
C6—C5—H5	121.1	C14—C13—H13	120.6
C7—C6—C5	119.2 (5)	N3—C14—C13	123.3 (5)
C7—C6—H6	120.4	N3—C14—H14	118.3
C5—C6—H6	120.4	C13—C14—H14	118.3
C8—C7—C6	118.6 (6)		
C1 ⁱ —N1—C2—C1	-0.5 (6)	C5—C6—C7—C8	-2.0 (12)
C1 ⁱ —N1—C2—C9	-179.4 (4)	C4—N2—C8—C7	-0.3 (10)
N1 ⁱ —C1—C2—N1	0.5 (7)	C6—C7—C8—N2	2.0 (12)
C3—C1—C2—N1	178.5 (4)	N1—C2—C9—S2	101.6 (4)
N1 ⁱ —C1—C2—C9	179.4 (4)	C1—C2—C9—S2	-77.3 (5)
C3—C1—C2—C9	-2.6 (6)	C10—S2—C9—C2	139.0 (3)
N1 ⁱ —C1—C3—S1	-49.8 (5)	C14—N3—C10—C11	0.8 (7)
C2—C1—C3—S1	132.0 (4)	C14—N3—C10—S2	-179.3 (4)
C4—S1—C3—C1	-155.3 (3)	C9—S2—C10—N3	-11.3 (4)
C8—N2—C4—C5	-1.4 (9)	C9—S2—C10—C11	168.6 (4)
C8—N2—C4—S1	178.8 (4)	N3—C10—C11—C12	-0.3 (7)
C3—S1—C4—N2	5.4 (5)	S2—C10—C11—C12	179.9 (4)
C3—S1—C4—C5	-174.4 (5)	C10—C11—C12—C13	-0.1 (8)
N2—C4—C5—C6	1.3 (9)	C11—C12—C13—C14	-0.1 (8)
S1—C4—C5—C6	-178.9 (5)	C10—N3—C14—C13	-1.1 (8)
C4—C5—C6—C7	0.5 (11)	C12—C13—C14—N3	0.7 (8)

Symmetry code: (i) $-x+2, -y+1, -z+2$.

Hydrogen-bond geometry (\AA , $^\circ$)

Cg2 is the centroid of pyridine ring N2/C4—C8.

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C11—H11 \cdots Cg2 ⁱⁱ	0.93	2.93	3.804 (6)	156

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