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Synthesis and structure of 1-*{(E)-[(6-methoxy- pyridin-2-yl)methylidene]amino}*-3-phenylthiourea

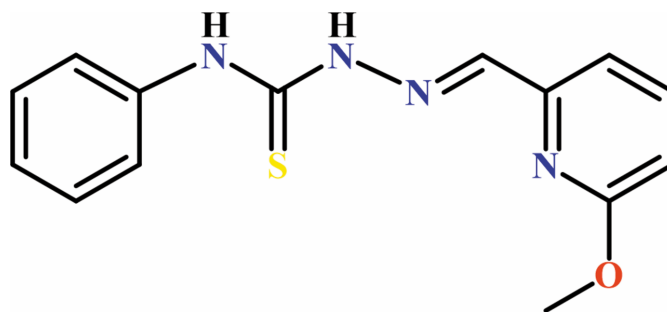
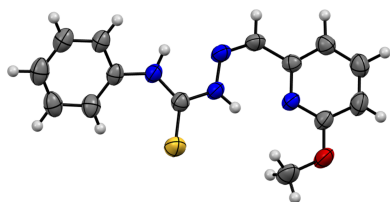
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The title compound, C₁₄H₁₄N₄OS, was crystallized at −20 °C by ether diffusion into an ethanol solution. The dihedral angle between the planes of the aromatic rings is 38.19 (19)° and the molecular conformation is supported by two intramolecular N—H···N hydrogen bonds. In the extended structure, N—H···O hydrogen bonds link the molecules into [011̄] chains. Hirshfeld surface analysis shows that H···H (44%), C···H/H···C (25%) and S···H/H···S (11.4%) contacts contribute the largest amounts.

1. Chemical context

Thiosemicarbazones, containing an —NH—(C=S)—NH=N— unit, are widely studied members of the Schiff base family: numerous articles discuss various synthetic strategies to prepare them and their applications, including optical devices, dyes, pharmaceuticals, biological activity, nanotechnology and catalytic activity (*e.g.* Nidhi *et al.*, 2025; Kumar *et al.*, 2022; Shahzad Munawar *et al.*, 2018). The addition of a pyridin-2-yl moiety to these thiosemicarbazide frameworks can make them more effective in biological applications, such as anticancer, antimicrobial, antifungal, antiviral and antibacterial activities (Zaware *et al.*, 2025).

Triapine (3-aminopyridine-2-carboxaldehyde thiosemicarbazone; C₇H₉N₅S), an α -*N*-pyridylthiosemicarbazone, is a potent ribonucleotide reductase (RR) inhibitor currently undergoing clinical trials (Finch *et al.*, 1999), which is believed to function by chelating iron ions. COTI-2 is a third-generation thiosemicarbazone that has received FDA (US Food and Drug Administration) orphan drug designation for ovarian cancer. It is undergoing phase 1 clinical trials (Lindemann *et al.*, 2019). Several metal–Schiff base complexes are being studied for their various biological activities (Bajaj *et al.*, 2021; Pervaiz *et al.*, 2024; Jiang *et al.*, 2024; Karpagam *et al.*, 2022).



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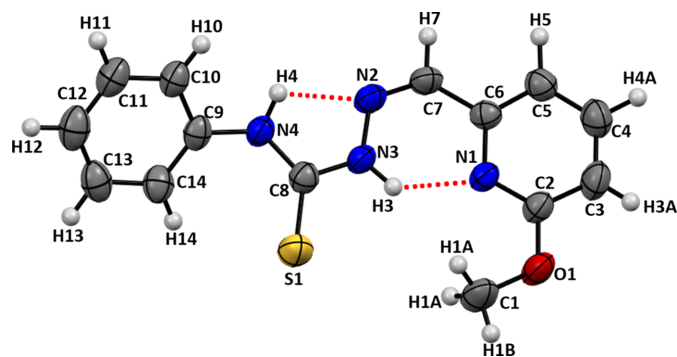


Figure 1

The molecular structure of (**I**), with displacement ellipsoids drawn at the 50% probability level. Intramolecular N—H···N hydrogen bonds are shown as red dashed lines.

As part of our work in this area, we now describe the synthesis, structure and Hirshfeld surface of the title thiosemicarbazone, 1-[(*E*)-[(6-methoxypyridin-2-yl)methylidene]-amino]-3-phenylthiourea (**I**), formed from the condensation reaction of 6-methoxypyridine-2-carboxaldehyde and 4-phenyl thiosemicarbazide.

2. Structural commentary

Compound (**I**) consists of an *o*-substituted pyridyl–Schiff base moiety connected to the phenyl-substituted thiosemicarbazide unit through an azomethine bond. It crystallizes in the orthorhombic space group *Pna*2₁, with one molecule in the asymmetric unit, as illustrated in Fig. 1. The compound contains three main structural fragments, a methoxy-substituted pyridine ring, an imine linkage and a phenylthiosemicarbazide group. The imine bond, with a C7=N2 bond length of 1.287 (5) Å, adopts the expected *E* configuration for the carbon–nitrogen bond, where the pyridyl ring is placed *trans* to the thiosemicarbazide N atom. The central chain

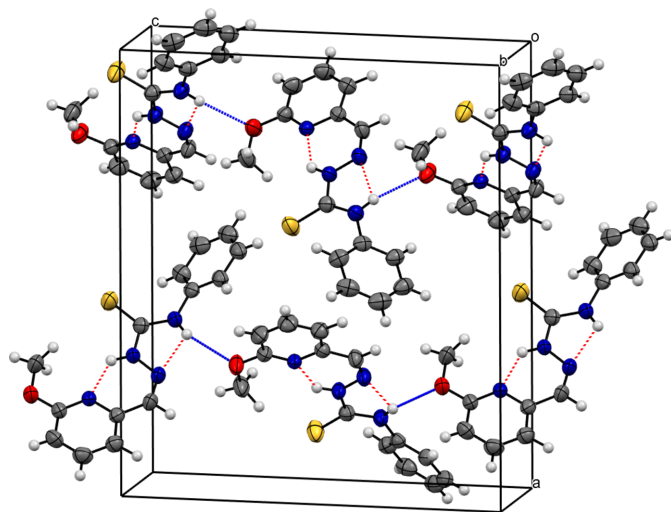


Figure 2

The packing diagram of (**I**), with intramolecular N—H···N hydrogen bonds shown as red dashed lines and intermolecular N—H···O hydrogen bonds shown as blue dashed lines.

Table 1

Hydrogen-bond geometry (Å, °).

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
N3—H3···N1	0.89 (3)	1.99 (4)	2.662 (4)	131 (3)
N4—H4···N2	0.91 (4)	2.07 (5)	2.576 (5)	114 (4)
N4—H4···O1 ⁱ	0.91 (4)	2.38 (5)	3.230 (4)	155 (3)
C14—H14···S1	0.97 (3)	2.78 (3)	3.249 (5)	110 (2)

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

adopts an extended conformation that allows partial electronic delocalization across the pyridine—C=N—N—C(=S)—NH—phenyl framework, as discussed previously for aryl-containing thiosemicarbazones (Palenik *et al.*, 1974). The N3—N2 bond length in the thiosemicarbazide part is 1.360 (4) Å, which is shorter than the expected N—N single bond length (1.45 Å). Also, the C6—C7 bond length is 1.461 (5) Å, which is shorter than the usual C—C single bond length (1.54 Å), which suggests a partial double-bond character due to the conjugation with the imine group (Bhatia *et al.*, 1977). Conversely, the thiocarbonyl bond, represented by C8—S1, shows a bond length of 1.658 (4) Å, which is longer than a typical C=S double bond length (1.56 Å), but much shorter than a typical C—S single bond length of 1.82 Å: this also confirms the extensive conjugation within the system.

The dihedral angle between the C2—C6/N1 and C9—C14 aromatic rings is 38.19 (19)°. The C atom of the methoxy group attached to the *ortho* position of the pyridine ring is approximately coplanar with the aromatic ring [displacement = 0.080 (6) Å] and the N1—C2—O1 and C3—C2—O1 bond angles are 118.5 (3) and 117.1 (3)°, respectively. The C2(aryl)—O1 bond length is 1.353 (4) Å, whereas the O1—C1(methyl) bond length is 1.429 (5) Å: this difference is typical for methoxy-substituted aromatic systems (Jones & Shaw, 1992). Two intramolecular N—H···N hydrogen bonds (Table 1) help to consolidate the molecular conformation: the N3—H3···N1 hydrogen bond closes an *S*(6) ring and the N4—H4···N2 hydrogen bond an *S*(5) ring. A short C—H···S contact is also present.

3. Supramolecular features

In the extended structure, N4—H4···O1 hydrogen bonds link the molecules into *C*(10) [01 $\bar{1}$] chains (Fig. 2). This N—H group also forms an intramolecular hydrogen bond (see above) and the bond-angle sum at the H atom is 357°.

4. Hirshfeld surface analysis

The Hirshfeld surface analysis of (**I**) was performed using *CrystalExplorer* (Version 21.5; Spackman *et al.*, 2021) and the d_{norm} map is illustrated in Fig. 3, with the intense red spots corresponding to the donor and acceptor groups for the N—H···O hydrogen bond. Two-dimensional fingerprint plots are shown in Fig. 4. Interactions between the H atoms (H···H) show the largest contribution (~44%) to the Hirshfeld surface, with a distance range of $d_e + d_i \approx 2.5$ Å. Nearly 25% is contributed by C···H/H···C interactions. Similarly, 11.4, 6.2,

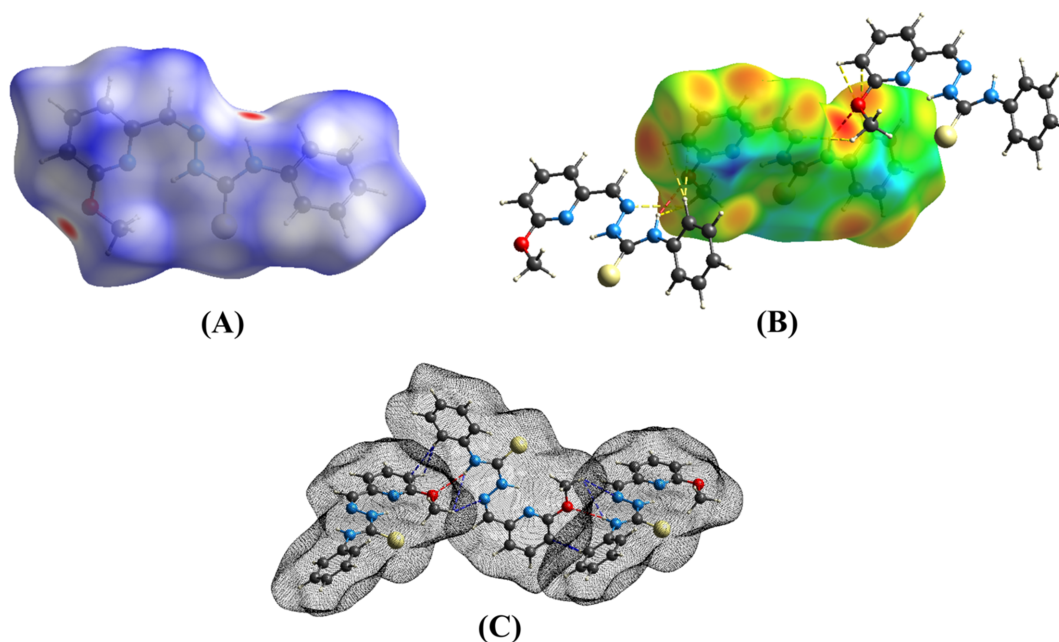


Figure 3
Hirshfeld surfaces of (I) mapped over (A) d_{norm} , (B) d_i and (C) d_{norm} (transparent Hirshfeld surface).

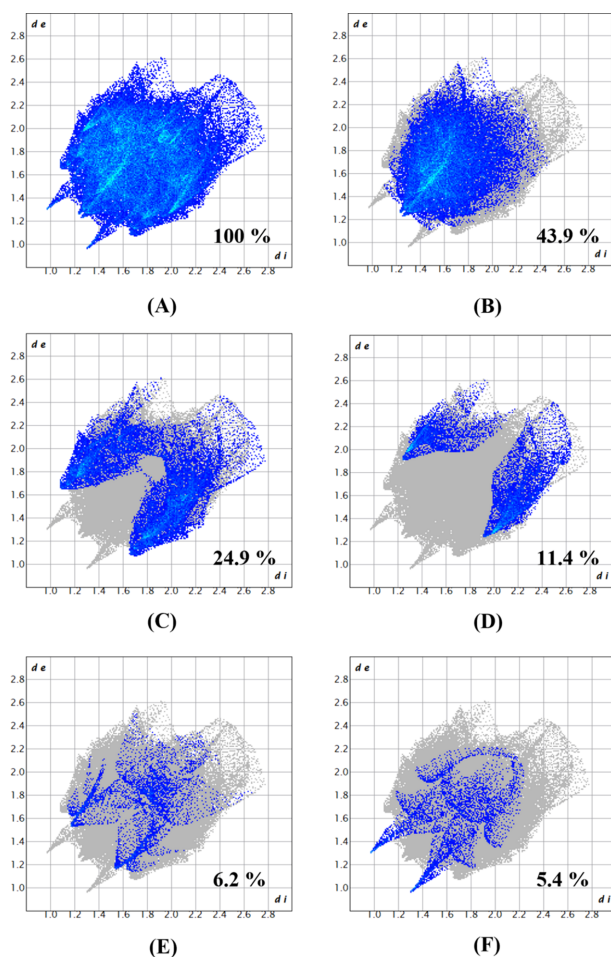


Figure 4
Two-dimensional fingerprint plots for (I): (a) all interactions; (b) H...H; (c) C...H/H...C; (d) S...H/H...S; (e) N...H/H...N; (f) O...H/H...O.

5.4, 4.7 and 1.4% of the interactions are contributed by S...H/H...H, H...S, N...H/H...N, O...H/H...O, C...N/N...C and S...C/C...S interactions, respectively. Finally, C...C, N...O/O...N and S...N/N...S interactions each contribute less than 1% to the contact surface.

5. Database survey

Several thiosemicarbazones have been reported in the literature, but only two structures have a 6-substituted pyridine moiety, *viz.* 6-methylpyridine-2-carbaldehyde-*N*(4)-phenylthiosemicarbazone and 6-bromo-2-formylpyridine-*N*(4)-phenylthiosemicarbazone (CSD refcodes BAFGAS and BAFGEW, respectively; Chumakov *et al.*, 2011).

6. Synthesis and crystallization

To 15 ml of a hot ethanolic solution of 6-methoxypyridine-2-carboxaldehyde (0.137 g, 1.00 mmol) with two added drops of glacial acetic acid, 4-phenylthiosemicarbazide (0.167 g, 1.00 mmol) dissolved in ethanol was added dropwise, and the mixture was refluxed for 2 h, which, on cooling to room temperature, gave a yellow precipitate. The obtained product was then recrystallised from ethanol solution by ether diffusion at $-20\text{ }^{\circ}\text{C}$ to give yellow needles of the title compound (yield 72%).

7. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

Acknowledgements

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Table 2

Experimental details.

Crystal data	
Chemical formula	C ₁₄ H ₁₄ N ₄ OS
<i>M_r</i>	286.35
Crystal system, space group	Orthorhombic, <i>Pna</i> 2 ₁
Temperature (K)	296
<i>a</i> , <i>b</i> , <i>c</i> (Å)	17.811 (4), 5.2400 (14), 15.340 (4)
<i>V</i> (Å ³)	1431.7 (6)
<i>Z</i>	4
Radiation type	Mo <i>K</i> α
μ (mm ⁻¹)	0.23
Crystal size (mm)	0.42 × 0.37 × 0.26
Data collection	
Diffractometer	Bruker
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	23242, 3409, 2258
<i>R</i> _{int}	0.078
(sin θ/λ) _{max} (Å ⁻¹)	0.660
Refinement	
<i>R</i> [[<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.040, 0.096, 1.02
No. of reflections	3409
No. of parameters	238
No. of restraints	1
H-atom treatment	All H-atom parameters refined
Δρ _{max} , Δρ _{min} (e Å ⁻³)	0.17, −0.16
Absolute structure	Flack <i>x</i> determined using 859 quotients [(<i>I</i> ⁺ − <i>I</i> [−])]/[(<i>I</i> ⁺ + <i>I</i> [−])] (Parsons <i>et al.</i> , 2013)
Absolute structure parameter	−0.04 (6)

Computer programs: *APEX3* and *SAINT* (Bruker, 2018), *SHELXT2014* (Sheldrick, 2015a), *SHELXL2018* (Sheldrick, 2015b), *Mercury* (Macrae *et al.*, 2020) and *publCIF* (Westrip, 2010).

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supporting information

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Synthesis and structure of 1-*{(E)-[(6-methoxypyridin-2-yl)methylidene]amino}*-3-phenylthiourea

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Computing details

1-*{(E)-[(6-Methoxypyridin-2-yl)methylidene]amino}*-3-phenylthiourea

Crystal data

C₁₄H₁₄N₄OS

M_r = 286.35

Orthorhombic, *Pna*2₁

a = 17.811 (4) Å

b = 5.2400 (14) Å

c = 15.340 (4) Å

V = 1431.7 (6) Å³

Z = 4

F(000) = 600

D_x = 1.328 Mg m⁻³

Mo *Kα* radiation, λ = 0.71073 Å

Cell parameters from 3409 reflections

θ = 2.3–28.0°

μ = 0.23 mm⁻¹

T = 296 K

Needle, yellow

0.42 × 0.37 × 0.26 mm

Data collection

Bruker

diffractometer

ω and phi scans

23242 measured reflections

3409 independent reflections

2258 reflections with *I* > 2σ(*I*)

*R*_{int} = 0.078

θ_{max} = 28.0°, θ_{min} = 2.3°

h = -23→23

k = -6→6

l = -20→20

Refinement

Refinement on *F*²

Least-squares matrix: full

R [*F*² > 2σ(*F*²)] = 0.040

wR(*F*²) = 0.096

S = 1.02

3409 reflections

238 parameters

1 restraint

Primary atom site location: dual

Hydrogen site location: difference Fourier map

All H-atom parameters refined

w = 1/[σ²(*F_o*²) + (0.0348*P*)² + 0.1169*P*]

where *P* = (*F_o*² + 2*F_c*²)/3

(Δ/σ)_{max} < 0.001

Δρ_{max} = 0.17 e Å⁻³

Δρ_{min} = -0.16 e Å⁻³

Extinction correction: SHELXL2018

(Sheldrick, 2015*b*),

*F_c** = *kF_c*[1 + 0.001*xF_c*²λ³/sin(2θ)]^{-1/4}

Extinction coefficient: 0.030 (3)

Absolute structure: Flack *x* determined using

859 quotients [(*I*⁺)-(*I*⁻)]/[(*I*⁺)+(*I*⁻)] (Parsons *et al.*, 2013)

Absolute structure parameter: -0.04 (6)

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	0.40063 (6)	0.6279 (2)	0.58169 (8)	0.0694 (4)
N1	0.21315 (14)	0.0452 (5)	0.58787 (19)	0.0431 (6)
N3	0.29424 (17)	0.3856 (6)	0.4999 (2)	0.0479 (7)
O1	0.22148 (15)	-0.0365 (6)	0.73431 (15)	0.0662 (9)
N2	0.25657 (17)	0.3109 (7)	0.4272 (2)	0.0538 (8)
N4	0.36505 (17)	0.6321 (6)	0.4102 (2)	0.0483 (7)
C2	0.1914 (2)	-0.0897 (7)	0.6554 (2)	0.0486 (9)
C9	0.4233 (2)	0.7937 (7)	0.3791 (2)	0.0454 (8)
C8	0.3525 (2)	0.5529 (6)	0.4928 (2)	0.0463 (8)
C6	0.1817 (2)	-0.0119 (7)	0.5095 (2)	0.0439 (8)
C10	0.4548 (2)	0.7346 (8)	0.2986 (3)	0.0512 (9)
C11	0.5105 (2)	0.8881 (9)	0.2637 (3)	0.0585 (11)
C7	0.2064 (2)	0.1351 (8)	0.4338 (2)	0.0534 (9)
C3	0.1383 (2)	-0.2814 (9)	0.6519 (3)	0.0628 (11)
C14	0.4467 (2)	1.0090 (8)	0.4234 (3)	0.0547 (9)
C5	0.1280 (2)	-0.2000 (7)	0.5005 (3)	0.0531 (9)
C13	0.5027 (2)	1.1614 (8)	0.3869 (3)	0.0607 (11)
C12	0.5341 (3)	1.0994 (9)	0.3078 (3)	0.0654 (12)
C4	0.1065 (2)	-0.3363 (7)	0.5728 (4)	0.0621 (11)
C1	0.2800 (3)	0.1498 (13)	0.7369 (3)	0.0737 (14)
H10	0.441 (2)	0.584 (8)	0.269 (3)	0.067 (12)*
H4A	0.070 (2)	-0.481 (9)	0.568 (3)	0.085 (14)*
H13	0.515 (2)	1.312 (8)	0.418 (3)	0.066 (12)*
H14	0.423 (2)	1.057 (6)	0.478 (2)	0.047 (10)*
H3A	0.127 (2)	-0.373 (7)	0.698 (3)	0.059 (12)*
H5	0.105 (2)	-0.236 (8)	0.438 (3)	0.068 (12)*
H7	0.183 (2)	0.093 (7)	0.378 (3)	0.061 (11)*
H3	0.285 (2)	0.316 (7)	0.552 (2)	0.057 (11)*
H12	0.572 (3)	1.212 (8)	0.284 (3)	0.080 (13)*
H11	0.531 (3)	0.848 (8)	0.209 (4)	0.095 (17)*
H4	0.338 (3)	0.540 (7)	0.371 (3)	0.071 (13)*
H1A	0.321 (3)	0.107 (8)	0.687 (4)	0.096 (15)*
H1B	0.293 (3)	0.145 (8)	0.792 (3)	0.081 (15)*
H1C	0.258 (3)	0.319 (11)	0.722 (4)	0.096 (19)*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0726 (7)	0.0868 (7)	0.0489 (5)	-0.0254 (6)	-0.0119 (6)	0.0070 (6)

N1	0.0374 (14)	0.0560 (16)	0.0357 (13)	-0.0022 (12)	-0.0006 (14)	0.0066 (15)
N3	0.0458 (19)	0.0634 (18)	0.0344 (15)	-0.0129 (14)	-0.0020 (13)	0.0081 (15)
O1	0.0607 (19)	0.097 (2)	0.0404 (14)	-0.0231 (16)	-0.0035 (13)	0.0160 (15)
N2	0.0535 (19)	0.073 (2)	0.0353 (16)	-0.0123 (17)	-0.0057 (14)	0.0069 (15)
N4	0.0474 (18)	0.0577 (19)	0.0397 (16)	-0.0103 (15)	-0.0020 (13)	0.0102 (15)
C2	0.042 (2)	0.061 (2)	0.042 (2)	-0.0033 (17)	0.0007 (17)	0.0089 (18)
C9	0.0398 (17)	0.045 (2)	0.051 (2)	0.0035 (16)	-0.0027 (16)	0.0145 (16)
C8	0.045 (2)	0.0474 (19)	0.0462 (19)	-0.0006 (17)	-0.0011 (16)	0.0043 (17)
C6	0.0400 (18)	0.049 (2)	0.0422 (18)	0.0011 (16)	-0.0021 (16)	-0.0016 (15)
C10	0.047 (2)	0.055 (2)	0.052 (2)	0.0010 (19)	0.0019 (18)	0.0135 (19)
C11	0.049 (2)	0.069 (3)	0.058 (2)	0.005 (2)	0.005 (2)	0.019 (2)
C7	0.056 (2)	0.067 (2)	0.0366 (18)	-0.010 (2)	-0.0080 (17)	0.0019 (18)
C3	0.056 (2)	0.070 (3)	0.062 (3)	-0.013 (2)	0.007 (2)	0.018 (2)
C14	0.054 (2)	0.046 (2)	0.064 (3)	0.0043 (18)	0.006 (2)	0.0062 (19)
C5	0.049 (2)	0.056 (2)	0.054 (2)	-0.0049 (19)	-0.0026 (18)	-0.003 (2)
C13	0.054 (2)	0.046 (2)	0.083 (3)	-0.0013 (19)	-0.009 (2)	0.012 (2)
C12	0.051 (3)	0.064 (3)	0.082 (3)	0.002 (2)	0.001 (2)	0.026 (3)
C4	0.053 (2)	0.060 (2)	0.073 (3)	-0.0134 (19)	-0.001 (2)	0.005 (2)
C1	0.068 (3)	0.108 (4)	0.045 (2)	-0.025 (3)	-0.015 (2)	0.013 (3)

Geometric parameters (Å, °)

S1—C8	1.658 (4)	C10—H10	0.94 (4)
N1—C2	1.312 (4)	C11—C12	1.364 (6)
N1—C6	1.360 (4)	C11—H11	0.93 (5)
N3—N2	1.360 (4)	C7—H7	0.97 (4)
N3—C8	1.363 (4)	C3—C4	1.369 (7)
N3—H3	0.89 (4)	C3—H3A	0.88 (4)
O1—C2	1.354 (4)	C14—C13	1.396 (6)
O1—C1	1.429 (5)	C14—H14	0.98 (4)
N2—C7	1.287 (5)	C5—C4	1.374 (7)
N4—C8	1.352 (4)	C5—H5	1.07 (4)
N4—C9	1.422 (5)	C13—C12	1.374 (6)
N4—H4	0.91 (5)	C13—H13	0.95 (4)
C2—C3	1.381 (5)	C12—H12	0.97 (5)
C9—C14	1.382 (6)	C4—H4A	1.00 (5)
C9—C10	1.390 (5)	C1—H1A	1.09 (5)
C6—C5	1.381 (5)	C1—H1B	0.88 (5)
C6—C7	1.461 (5)	C1—H1C	1.00 (6)
C10—C11	1.386 (6)		
C2—N1—C6	117.2 (3)	N2—C7—C6	130.5 (3)
N2—N3—C8	119.7 (3)	N2—C7—H7	113 (2)
N2—N3—H3	122 (2)	C6—C7—H7	116 (2)
C8—N3—H3	118 (2)	C4—C3—C2	118.0 (4)
C2—O1—C1	117.1 (3)	C4—C3—H3A	120 (3)
C7—N2—N3	118.9 (3)	C2—C3—H3A	121 (3)
C8—N4—C9	128.1 (3)	C9—C14—C13	119.0 (4)

C8—N4—H4	112 (3)	C9—C14—H14	120 (2)
C9—N4—H4	119 (3)	C13—C14—H14	121 (2)
N1—C2—O1	118.5 (3)	C4—C5—C6	118.9 (4)
N1—C2—C3	124.4 (4)	C4—C5—H5	122 (2)
O1—C2—C3	117.1 (3)	C6—C5—H5	119 (2)
C14—C9—C10	119.8 (4)	C12—C13—C14	120.7 (4)
C14—C9—N4	122.7 (4)	C12—C13—H13	124 (3)
C10—C9—N4	117.3 (3)	C14—C13—H13	116 (3)
N4—C8—N3	113.5 (3)	C11—C12—C13	120.3 (4)
N4—C8—S1	127.8 (3)	C11—C12—H12	121 (3)
N3—C8—S1	118.7 (3)	C13—C12—H12	118 (3)
N1—C6—C5	122.1 (3)	C3—C4—C5	119.4 (4)
N1—C6—C7	117.5 (3)	C3—C4—H4A	120 (3)
C5—C6—C7	120.4 (4)	C5—C4—H4A	121 (3)
C11—C10—C9	120.2 (4)	O1—C1—H1A	109 (3)
C11—C10—H10	119 (3)	O1—C1—H1B	102 (3)
C9—C10—H10	121 (3)	H1A—C1—H1B	119 (4)
C12—C11—C10	120.0 (4)	O1—C1—H1C	108 (3)
C12—C11—H11	120 (3)	H1A—C1—H1C	107 (4)
C10—C11—H11	120 (3)	H1B—C1—H1C	111 (5)
C8—N3—N2—C7	173.5 (4)	C9—C10—C11—C12	-0.7 (6)
C6—N1—C2—O1	-179.8 (3)	N3—N2—C7—C6	-1.3 (7)
C6—N1—C2—C3	-1.1 (5)	N1—C6—C7—N2	2.7 (7)
C1—O1—C2—N1	-5.3 (6)	C5—C6—C7—N2	-177.7 (4)
C1—O1—C2—C3	175.9 (4)	N1—C2—C3—C4	0.6 (6)
C8—N4—C9—C14	-41.6 (6)	O1—C2—C3—C4	179.3 (4)
C8—N4—C9—C10	141.5 (4)	C10—C9—C14—C13	-1.1 (5)
C9—N4—C8—N3	-176.2 (3)	N4—C9—C14—C13	-178.0 (3)
C9—N4—C8—S1	1.6 (6)	N1—C6—C5—C4	-1.0 (6)
N2—N3—C8—N4	1.5 (5)	C7—C6—C5—C4	179.4 (3)
N2—N3—C8—S1	-176.5 (3)	C9—C14—C13—C12	0.3 (6)
C2—N1—C6—C5	1.3 (5)	C10—C11—C12—C13	-0.2 (6)
C2—N1—C6—C7	-179.2 (3)	C14—C13—C12—C11	0.4 (6)
C14—C9—C10—C11	1.3 (5)	C2—C3—C4—C5	-0.3 (6)
N4—C9—C10—C11	178.4 (3)	C6—C5—C4—C3	0.5 (6)

Hydrogen-bond geometry (Å, °)

<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>
N3—H3 \cdots N1	0.89 (3)	1.99 (4)	2.662 (4)	131 (3)
N4—H4 \cdots N2	0.91 (4)	2.07 (5)	2.576 (5)	114 (4)
N4—H4 \cdots O1 ⁱ	0.91 (4)	2.38 (5)	3.230 (4)	155 (3)
C14—H14 \cdots S1	0.97 (3)	2.78 (3)	3.249 (5)	110 (2)

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