



Crystal structure of 3-methylpyridine-2-carbaldehyde 4-methylthiosemicarbazone monohydrate

Nur Shuhada Mohd Mokhtaruddin,^a Thahira Begum S. A. Ravoof,^{a*} Mohamed Ibrahim Mohamed Tahir^a and Edward R. T. Tiekink^b

^aDepartment of Chemistry, Universiti Putra Malaysia, 43400 Serdang, Malaysia, and

^bDepartment of Chemistry, University of Malaya, 50603 Kuala Lumpur, Malaysia.

*Correspondence e-mail: thahira@upm.edu.my

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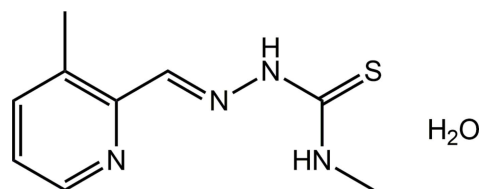
In the title hydrate, C₉H₁₂N₄S·H₂O (systematic name: 3-methyl-1-[(*E*)-(3-methylpyridin-2-yl)methylidene]amino)-thiourea monohydrate), a small twist is noted between the pyridine ring and the rest of the organic molecule [dihedral angle = 6.96 (5)°]. The imine and pyridine N atoms are *syn*, and the amine H atoms are *anti*. The latter arrangement allows for the formation of an intramolecular N—H...N(imine) hydrogen bond. Both the N-bonded H atoms form hydrogen bonds to symmetry-related water molecules, and the latter forms O—H hydrogen bonds with the pyridine N and thione S atoms. These interactions lead to supramolecular layers that stack along the *a*-axis direction with no specific interactions between them.

Keywords: crystal structure; hydrogen bonding; thiosemicarbazone.

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1. Related literature

For background to the coordination chemistry of thiosemicarbazones, see: Beraldo *et al.* (2001); Sreekanth *et al.* (2004). For the structure of the parent compound, in which the pyridine N atom is *anti* to the imine N atom, see: West *et al.* (1996). For the synthesis of the title compound, see: Ali *et al.* (1997).



2. Experimental

2.1. Crystal data

C ₉ H ₁₂ N ₄ S·H ₂ O	<i>V</i> = 1119.90 (6) Å ³
<i>M_r</i> = 226.30	<i>Z</i> = 4
Monoclinic, <i>P</i> 2 ₁ / <i>c</i>	Cu <i>K</i> α radiation
<i>a</i> = 10.4493 (3) Å	<i>μ</i> = 2.42 mm ⁻¹
<i>b</i> = 13.6989 (3) Å	<i>T</i> = 100 K
<i>c</i> = 8.0235 (3) Å	0.30 × 0.20 × 0.10 mm
<i>β</i> = 102.816 (3)°	

2.2. Data collection

Oxford Diffraction Xcaliber Eos Gemini diffractometer	14591 measured reflections
Absorption correction: multi-scan (<i>CrysAlis PRO</i> ; Agilent, 2011)	2160 independent reflections
<i>T_{min}</i> = 0.860, <i>T_{max}</i> = 1.000	2044 reflections with <i>I</i> > 2σ(<i>I</i>)
	<i>R_{int}</i> = 0.022

2.3. Refinement

<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)] = 0.034	H atoms treated by a mixture of independent and constrained refinement
<i>wR</i> (<i>F</i> ²) = 0.097	<i>Δρ_{max}</i> = 0.31 e Å ⁻³
<i>S</i> = 1.05	<i>Δρ_{min}</i> = -0.25 e Å ⁻³
2160 reflections	
150 parameters	
5 restraints	

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>
N4—H4N...N2	0.88 (2)	2.19 (2)	2.6116 (16)	109 (1)
N1—H1N...O1W ⁱ	0.88 (1)	2.12 (1)	2.9940 (15)	170 (2)
N4—H4N...O1W	0.88 (2)	2.50 (2)	3.3100 (15)	154 (1)
O1W—H1W...N3	0.84 (2)	2.11 (2)	2.9371 (16)	172 (2)
O1W—H2W...S1 ⁱⁱ	0.85 (2)	2.50 (2)	3.3412 (11)	173 (2)

Symmetry codes: (i) $-x + 1, y + \frac{1}{2}, -z + \frac{3}{2}$; (ii) $x, -y + \frac{3}{2}, z + \frac{1}{2}$.

Data collection: *CrysAlis PRO* (Agilent, 2011); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis PRO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2015); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012) and *DIAMOND* (Brandenburg, 2006); software used to prepare material for publication: *publCIF* (Westrip, 2010).

Acknowledgements

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Supporting information for this paper is available from the IUCr electronic archives (Reference: HB7381).

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supporting information

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S1. Refinement

S2. Experimental

The Schiff base ligand was prepared according to Ali *et al.* (1997). 4-Methyl-3-thiosemicarbazide (0.01 mol) was dissolved in hot 95% ethanol (50 ml), and an equimolar amount of 3-methylpyridine-2-carbaldehyde in the same solvent (20 ml) was added. The mixture was heated with occasional stirring until the volume reduced to 20 ml. It was allowed to stand overnight and a yellow precipitate formed, which was filtered off and washed with cold ethanol. Crystals suitable for X-ray diffraction analysis were obtained by recrystallization from ethanol. Yields were high, *ca.* 92%.

S3. Refinement

Carbon-bound H-atoms were placed in calculated positions (C—H = 0.95 to 0.98 Å) and were included in the refinement in the riding model approximation with $U_{\text{iso}}(\text{H}) = 1.2\text{--}1.5U_{\text{eq}}(\text{C})$. The O—H atoms were refined with O—H = 0.84±0.01 Å, and with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$. The N—H H atoms were treated similarly with N—H = 0.88±0.01 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{N})$.

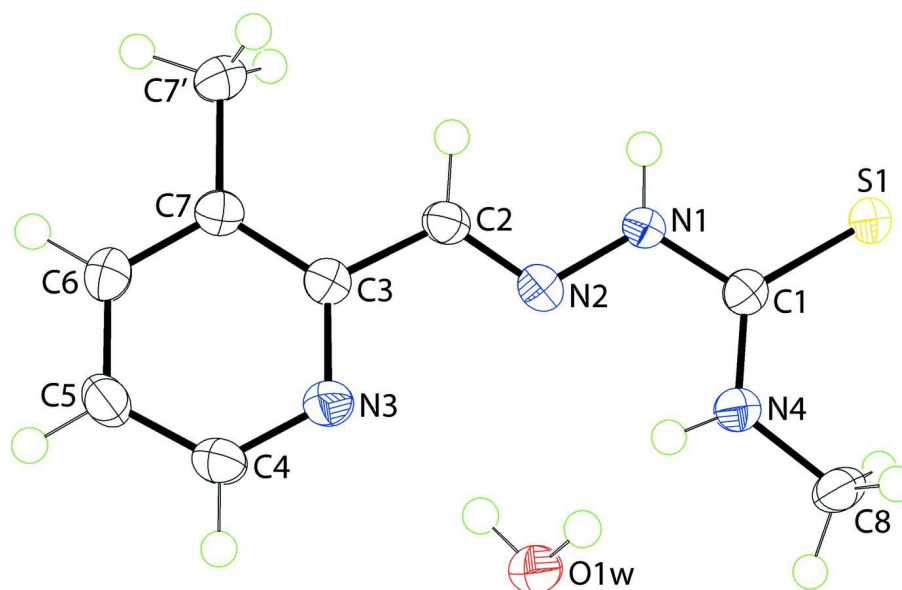


Figure 1

The molecular structure of the title compound showing the atom-labelling scheme and displacement ellipsoids at the 70% probability level.

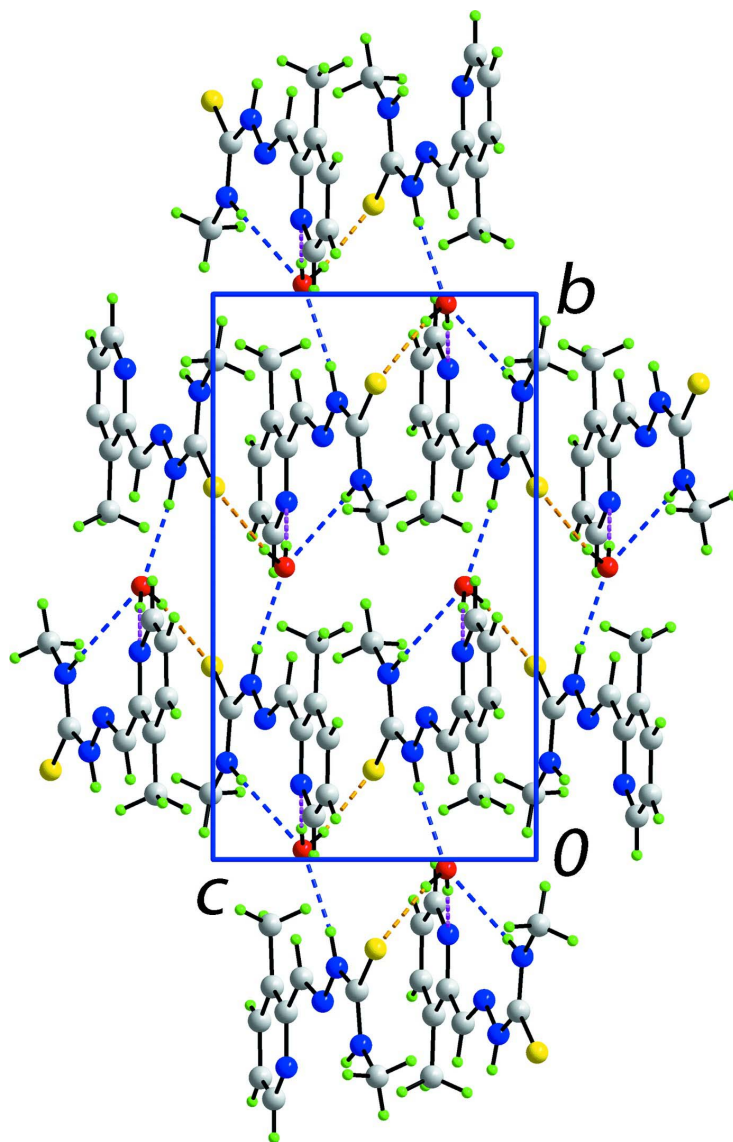


Figure 2

A view of the supramolecular layer in parallel to (1 0 0) sustained by N—H...O (blue dashed lines), O—H...N (pink) and O—H...S (orange) hydrogen bonding.

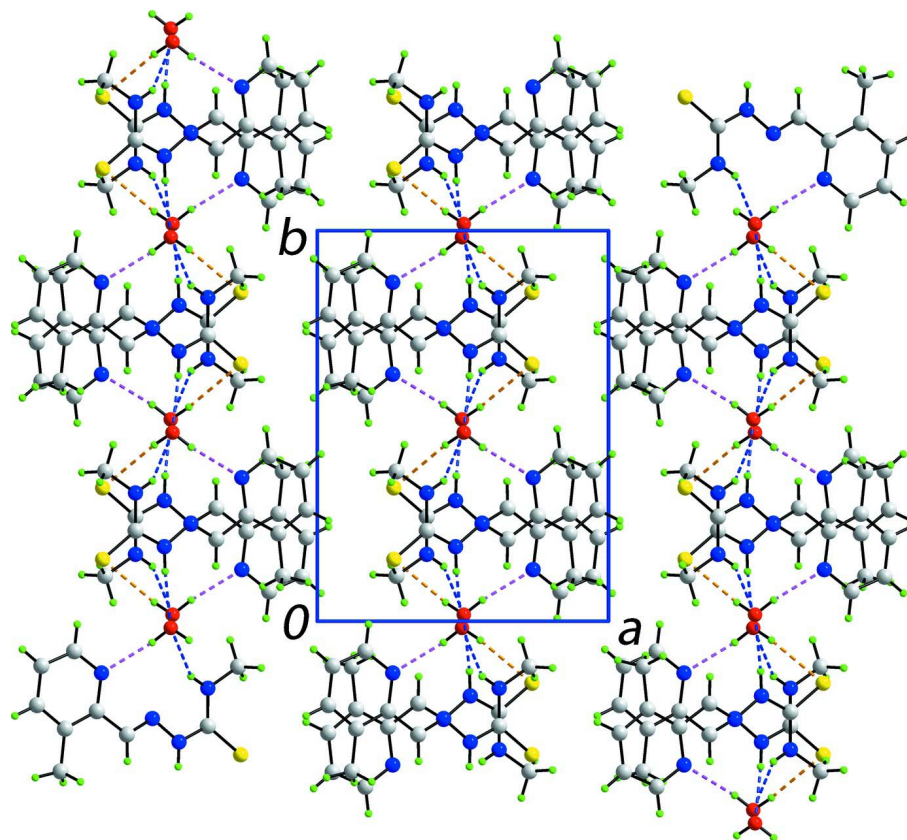


Figure 3

A view of the unit-cell contents in projection down the c axis. The N—H \cdots O (blue), O—H \cdots N (pink) and O—H \cdots S (orange) hydrogen bonds are shown as dashed lines.

3-Methyl-1- $\{$ (E)-[3-methylpyridin-2-yl)methylidene]amino $\}$ thiourea monohydrate

Crystal data

$C_9H_{12}N_4S \cdot H_2O$

$M_r = 226.30$

Monoclinic, $P2_1/c$

$a = 10.4493$ (3) Å

$b = 13.6989$ (3) Å

$c = 8.0235$ (3) Å

$\beta = 102.816$ (3)°

$V = 1119.90$ (6) Å³

$Z = 4$

$F(000) = 480$

$D_x = 1.342$ Mg m⁻³

Cu $K\alpha$ radiation, $\lambda = 1.5418$ Å

Cell parameters from 7855 reflections

$\theta = 3.2$ – 71.2 °

$\mu = 2.42$ mm⁻¹

$T = 100$ K

Prism, pale-brown

$0.30 \times 0.20 \times 0.10$ mm

Data collection

Oxford Diffraction Xcaliber Eos Gemini diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

Detector resolution: 16.1952 pixels mm⁻¹

ω scans

Absorption correction: multi-scan

(*CrysAlis PRO*; Agilent, 2011)

$T_{\min} = 0.860$, $T_{\max} = 1.000$

14591 measured reflections

2160 independent reflections

2044 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.022$

$\theta_{\max} = 71.4$ °, $\theta_{\min} = 4.3$ °

$h = -12 \rightarrow 12$

$k = -16 \rightarrow 16$

$l = -9 \rightarrow 9$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.034$
 $wR(F^2) = 0.097$
 $S = 1.05$
 2160 reflections
 150 parameters
 5 restraints

Hydrogen site location: mixed
 H atoms treated by a mixture of independent
 and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0657P)^2 + 0.3425P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.31 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.25 \text{ e } \text{\AA}^{-3}$

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s 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	0.73687 (3)	0.84153 (2)	0.49693 (4)	0.01984 (14)
N1	0.52525 (11)	0.80894 (8)	0.61677 (14)	0.0178 (3)
H1N	0.5225 (16)	0.8721 (7)	0.636 (2)	0.021*
N2	0.43392 (11)	0.74878 (8)	0.66067 (14)	0.0178 (3)
N3	0.25907 (11)	0.63228 (8)	0.77276 (14)	0.0199 (3)
N4	0.62430 (11)	0.67137 (8)	0.54238 (14)	0.0187 (3)
H4N	0.5662 (14)	0.6409 (12)	0.588 (2)	0.022*
C1	0.62415 (13)	0.76805 (9)	0.55465 (16)	0.0168 (3)
C2	0.34637 (13)	0.78964 (9)	0.72608 (16)	0.0177 (3)
H2	0.3482	0.8582	0.7437	0.021*
C3	0.24297 (13)	0.73011 (10)	0.77382 (16)	0.0168 (3)
C4	0.16527 (14)	0.57657 (10)	0.81199 (18)	0.0228 (3)
H4	0.1760	0.5077	0.8116	0.027*
C5	0.05263 (14)	0.61413 (10)	0.85338 (18)	0.0224 (3)
H5	-0.0125	0.5719	0.8792	0.027*
C6	0.03765 (13)	0.71450 (10)	0.85609 (17)	0.0211 (3)
H6	-0.0381	0.7420	0.8848	0.025*
C7	0.13356 (13)	0.77500 (9)	0.81675 (16)	0.0177 (3)
C7'	0.11857 (15)	0.88417 (10)	0.8229 (2)	0.0270 (3)
H7'1	0.0318	0.9001	0.8432	0.040*
H7'2	0.1274	0.9125	0.7139	0.040*
H7'3	0.1867	0.9109	0.9158	0.040*
C8	0.72818 (13)	0.61612 (11)	0.49226 (17)	0.0225 (3)
H8A	0.7460	0.6438	0.3871	0.034*
H8B	0.7008	0.5479	0.4724	0.034*
H8C	0.8079	0.6194	0.5834	0.034*
O1W	0.49697 (10)	0.51694 (7)	0.77859 (13)	0.0232 (2)
H1W	0.4330 (14)	0.5544 (12)	0.774 (2)	0.035*
H2W	0.5595 (14)	0.5483 (13)	0.841 (2)	0.035*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0178 (2)	0.0182 (2)	0.0254 (2)	-0.00111 (11)	0.00872 (14)	-0.00060 (11)
N1	0.0179 (6)	0.0137 (5)	0.0231 (6)	-0.0011 (4)	0.0075 (5)	-0.0007 (4)
N2	0.0173 (6)	0.0177 (5)	0.0179 (6)	-0.0021 (4)	0.0030 (4)	0.0011 (4)
N3	0.0194 (6)	0.0163 (5)	0.0238 (6)	0.0013 (4)	0.0045 (5)	0.0013 (4)
N4	0.0197 (6)	0.0163 (6)	0.0210 (6)	0.0006 (4)	0.0060 (5)	0.0001 (4)
C1	0.0163 (6)	0.0182 (6)	0.0152 (6)	0.0009 (5)	0.0017 (5)	0.0002 (5)
C2	0.0181 (6)	0.0146 (6)	0.0197 (6)	-0.0005 (5)	0.0029 (5)	0.0006 (5)
C3	0.0164 (6)	0.0175 (6)	0.0154 (6)	0.0000 (5)	0.0015 (5)	0.0005 (5)
C4	0.0244 (7)	0.0159 (6)	0.0282 (7)	-0.0005 (5)	0.0061 (6)	0.0023 (5)
C5	0.0208 (7)	0.0205 (7)	0.0266 (7)	-0.0044 (5)	0.0066 (5)	0.0025 (5)
C6	0.0174 (6)	0.0238 (7)	0.0226 (7)	0.0010 (5)	0.0055 (5)	-0.0003 (5)
C7	0.0184 (6)	0.0168 (7)	0.0172 (6)	0.0002 (5)	0.0024 (5)	0.0002 (5)
C7'	0.0292 (8)	0.0172 (7)	0.0385 (8)	0.0030 (6)	0.0161 (6)	-0.0008 (6)
C8	0.0217 (7)	0.0187 (7)	0.0261 (7)	0.0051 (5)	0.0036 (6)	-0.0024 (5)
O1W	0.0207 (5)	0.0180 (5)	0.0309 (5)	0.0003 (4)	0.0055 (4)	-0.0032 (4)

Geometric parameters (Å, °)

S1—C1	1.6903 (13)	C4—H4	0.9500
N1—C1	1.3633 (17)	C5—C6	1.385 (2)
N1—N2	1.3649 (15)	C5—H5	0.9500
N1—H1N	0.881 (9)	C6—C7	1.3896 (19)
N2—C2	1.2801 (18)	C6—H6	0.9500
N3—C4	1.3338 (18)	C7—C7'	1.5057 (18)
N3—C3	1.3510 (17)	C7'—H7'1	0.9800
N4—C1	1.3281 (17)	C7'—H7'2	0.9800
N4—C8	1.4513 (17)	C7'—H7'3	0.9800
N4—H4N	0.879 (9)	C8—H8A	0.9800
C2—C3	1.4706 (18)	C8—H8B	0.9800
C2—H2	0.9500	C8—H8C	0.9800
C3—C7	1.4066 (18)	O1W—H1W	0.836 (9)
C4—C5	1.391 (2)	O1W—H2W	0.848 (9)
C1—N1—N2	118.45 (11)	C6—C5—H5	120.8
C1—N1—H1N	121.7 (11)	C4—C5—H5	120.8
N2—N1—H1N	119.6 (11)	C5—C6—C7	119.93 (13)
C2—N2—N1	116.49 (11)	C5—C6—H6	120.0
C4—N3—C3	117.84 (12)	C7—C6—H6	120.0
C1—N4—C8	123.63 (12)	C6—C7—C3	117.47 (12)
C1—N4—H4N	115.5 (12)	C6—C7—C7'	119.96 (12)
C8—N4—H4N	119.7 (11)	C3—C7—C7'	122.58 (12)
N4—C1—N1	116.76 (12)	C7—C7'—H7'1	109.5
N4—C1—S1	124.14 (10)	C7—C7'—H7'2	109.5
N1—C1—S1	119.10 (10)	H7'1—C7'—H7'2	109.5
N2—C2—C3	119.83 (12)	C7—C7'—H7'3	109.5

N2—C2—H2	120.1	H7'1—C7'—H7'3	109.5
C3—C2—H2	120.1	H7'2—C7'—H7'3	109.5
N3—C3—C7	122.98 (12)	N4—C8—H8A	109.5
N3—C3—C2	116.66 (12)	N4—C8—H8B	109.5
C7—C3—C2	120.36 (12)	H8A—C8—H8B	109.5
N3—C4—C5	123.36 (13)	N4—C8—H8C	109.5
N3—C4—H4	118.3	H8A—C8—H8C	109.5
C5—C4—H4	118.3	H8B—C8—H8C	109.5
C6—C5—C4	118.41 (12)	H1W—O1W—H2W	102.7 (18)
C1—N1—N2—C2	176.76 (11)	C3—N3—C4—C5	0.1 (2)
C8—N4—C1—N1	-174.76 (11)	N3—C4—C5—C6	-0.8 (2)
C8—N4—C1—S1	5.79 (18)	C4—C5—C6—C7	0.5 (2)
N2—N1—C1—N4	-0.36 (17)	C5—C6—C7—C3	0.53 (19)
N2—N1—C1—S1	179.12 (9)	C5—C6—C7—C7'	-178.83 (12)
N1—N2—C2—C3	178.85 (11)	N3—C3—C7—C6	-1.32 (19)
C4—N3—C3—C7	1.02 (19)	C2—C3—C7—C6	178.27 (12)
C4—N3—C3—C2	-178.58 (11)	N3—C3—C7—C7'	178.02 (12)
N2—C2—C3—N3	11.03 (18)	C2—C3—C7—C7'	-2.39 (19)
N2—C2—C3—C7	-168.58 (12)		

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

<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>
N4—H4N \cdots N2	0.88 (2)	2.19 (2)	2.6116 (16)	109 (1)
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