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 1,3-Di-*n*-butylthiourea

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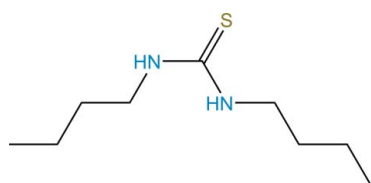
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 Key indicators: single-crystal X-ray study; $T = 120$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å; R factor = 0.046; wR factor = 0.116; data-to-parameter ratio = 18.9.

In the title compound, $\text{C}_9\text{H}_{20}\text{N}_2\text{S}$, the *n*-butyl groups are in *syn* and *anti* positions in relation to the $\text{C}=\text{S}$ bond. In the crystal, two molecules are connected by two $\text{N}-\text{H}\cdots\text{S}=\text{C}$ hydrogen bonds into a centrosymmetric dimer. Another $\text{N}-\text{H}\cdots\text{S}=\text{C}$ hydrogen bond links the dimers, forming layers with a hydrophilic interior and a hydrophobic exterior, which spread across the (100) plane. Interlacing of the external butyl groups combines these layers into a three-dimensional structure.

Related literature

For structures of *N,N'*-di-*n*-butylthiourea complexes with mercury and copper, see: Ahmad *et al.* (2009); Khan *et al.* (2007); Warda (1998). For structures of other symmetrically substituted thiourea derivatives, see: Custelcean *et al.* (2005); Djurdjevic *et al.* (2007); Ramnathan *et al.* (1995). For synthetic methods, see: Herr *et al.* (2000); Kricheldorf (1970); Ranu *et al.* (2003).



Experimental

Crystal data

$\text{C}_9\text{H}_{20}\text{N}_2\text{S}$
 $M_r = 188.33$
 Monoclinic, $P2_1/c$
 $a = 12.6395$ (6) Å
 $b = 10.0836$ (6) Å
 $c = 9.0128$ (5) Å
 $\beta = 90.476$ (5)°

$V = 1148.66$ (11) Å³
 $Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 0.24$ mm⁻¹
 $T = 120$ K
 $0.48 \times 0.29 \times 0.09$ mm

Data collection

Oxford Diffraction Xcalibur
 Sapphire2 diffractometer
 Absorption correction: analytical
 [CrysAlis PRO (Oxford

Diffraction, 2010; based on
 Clark & Reid, 1995)]
 $T_{\min} = 0.94$, $T_{\max} = 0.978$
 5268 measured reflections

2247 independent reflections
 1656 reflections with $I > 2\sigma(I)$

 $R_{\text{int}} = 0.038$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.046$
 $wR(F^2) = 0.116$
 $S = 0.97$
 2247 reflections
 119 parameters
 2 restraints

H atoms treated by a mixture of
 independent and constrained
 refinement
 $\Delta\rho_{\text{max}} = 0.45$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.27$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{N1}-\text{H1}\cdots\text{S1}^{\text{i}}$	0.84 (1)	2.58 (1)	3.3943 (17)	164 (2)
$\text{N2}-\text{H2}\cdots\text{S1}^{\text{ii}}$	0.85 (1)	2.52 (1)	3.3319 (17)	159 (2)

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

Data collection: *CrysAlis PRO* (Oxford Diffraction, 2010); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis PRO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *OLEX2* (Dolomanov *et al.*, 2009) and *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *WinGX* (Farrugia, 1999) and *PLATON* (Spek, 2009).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SI2344).

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1,3-Di-*n*-butylthiourea

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S1. Comment

N,N'-Di-*n*-butylthiourea, S=C(NH^{*n*}Bu)₂, is commonly used as a vulcanization accelerator in rubber processing, as an insecticide, as an additive to fertilizers, as a corrosion inhibitor, as an agent for metal treatments, *etc.*

No X-ray structure of pure compound was known until now, although the Cambridge Structural Database contains data on its mercury(ii) (Ahmad *et al.*, 2009), copper(i) (Khan *et al.*, 2007) and copper(ii) (Warda, 1998) complexes. In their structures one of the *n*-butyl groups of *N,N'*-di-*n*-butylthiourea molecule is in the *syn* position and the second is in the *anti* position in relation to the C=S bond. The same conformation is present in the title compound and this allows the formation of the centrosymmetric dimers (see Fig. 1) held together by two N1—H···S1ⁱ=C1ⁱ hydrogen bonds [symmetry code: (i): $-x, -y + 1, -z + 2$]. Namely, motif **R**₂²(8) is formed. Furthermore, there are additional N2—H···S1ⁱⁱ=C1ⁱⁱ hydrogen bonds [symmetry code: (ii): $x, -y + 3/2, z - 1/2$], which link the dimers to form the two-dimensional layers (see Fig. 2). Hydrogen bonds parameters are summarized in Tab. 1. Hydrocarbon chains pointing outside the layer interact with those from the neighbouring ones by van der Waals forces to form a three-dimensional crystal structure. The same packing patterns can be found in *syn,anti* isomers of other analogues: *N,N'*-diethylthiourea and *N,N'*-diisopropylthiourea (Ramnathan *et al.*, 1995) and similar in *N,N'*-bis(prop-2-en-1-yl)thiourea (Djurdjevic *et al.*, 2007). The case of *N,N'*-di-*tert*-butylthiourea is different, because the molecules adopt *syn,syn* conformation (Custelcean *et al.*, 2005).

There are several synthetic methods to obtain symmetrical thioureas. For example condensation of amine hydrochlorides with potassium thiocyanate (Herr *et al.*, 2000) or reaction of *N*-silylated amines with carbon disulfide (Kricheldorf, 1970). The very simple, quick and solvent-free method was proposed by Ranu *et al.* (2003) incorporating addition of amines to carbon disulfide on the surface of alumina under microwave irradiation. In the case of *n*-butylamine, mixture was irradiated for 2 minutes and the yield was 89%.

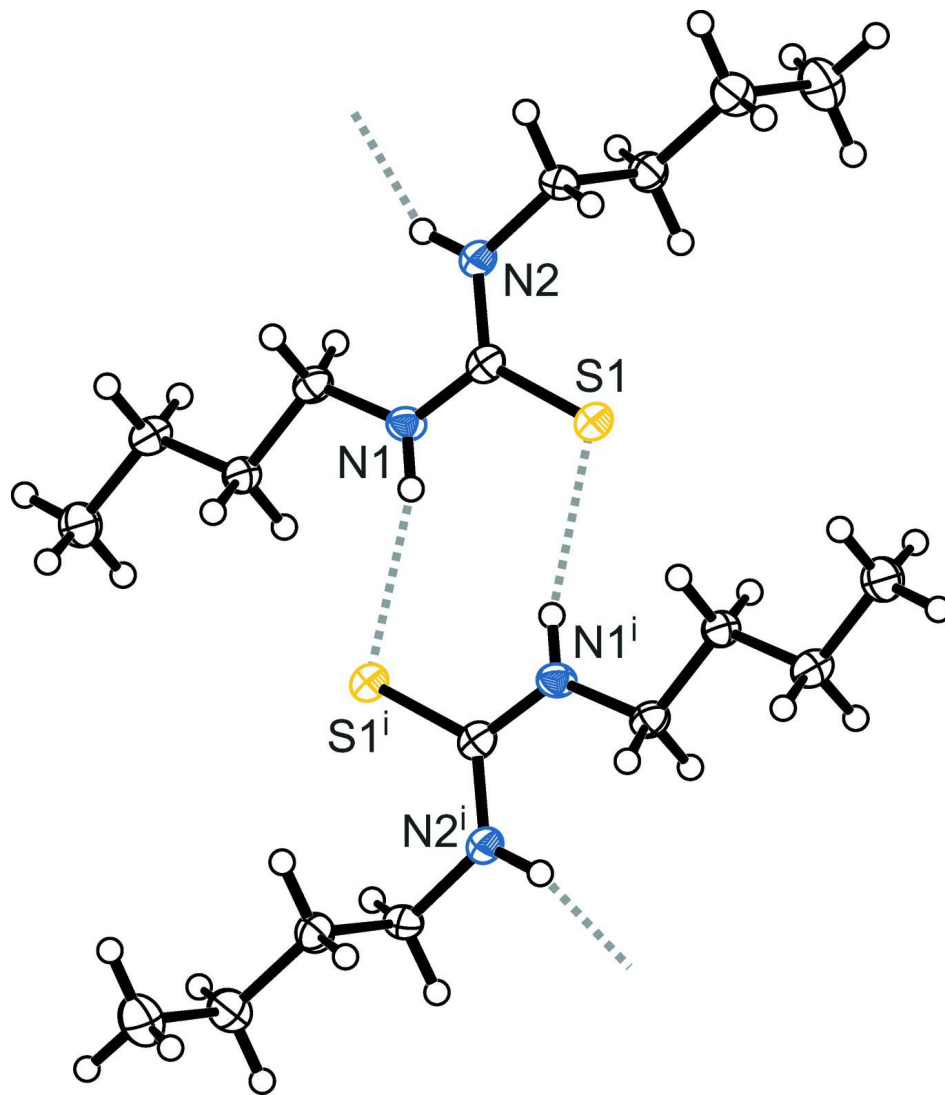
We found that good quality crystals can be obtained by recrystallization from ethyl acetate or acetylacetone (2,4-pentanedione).

S2. Experimental

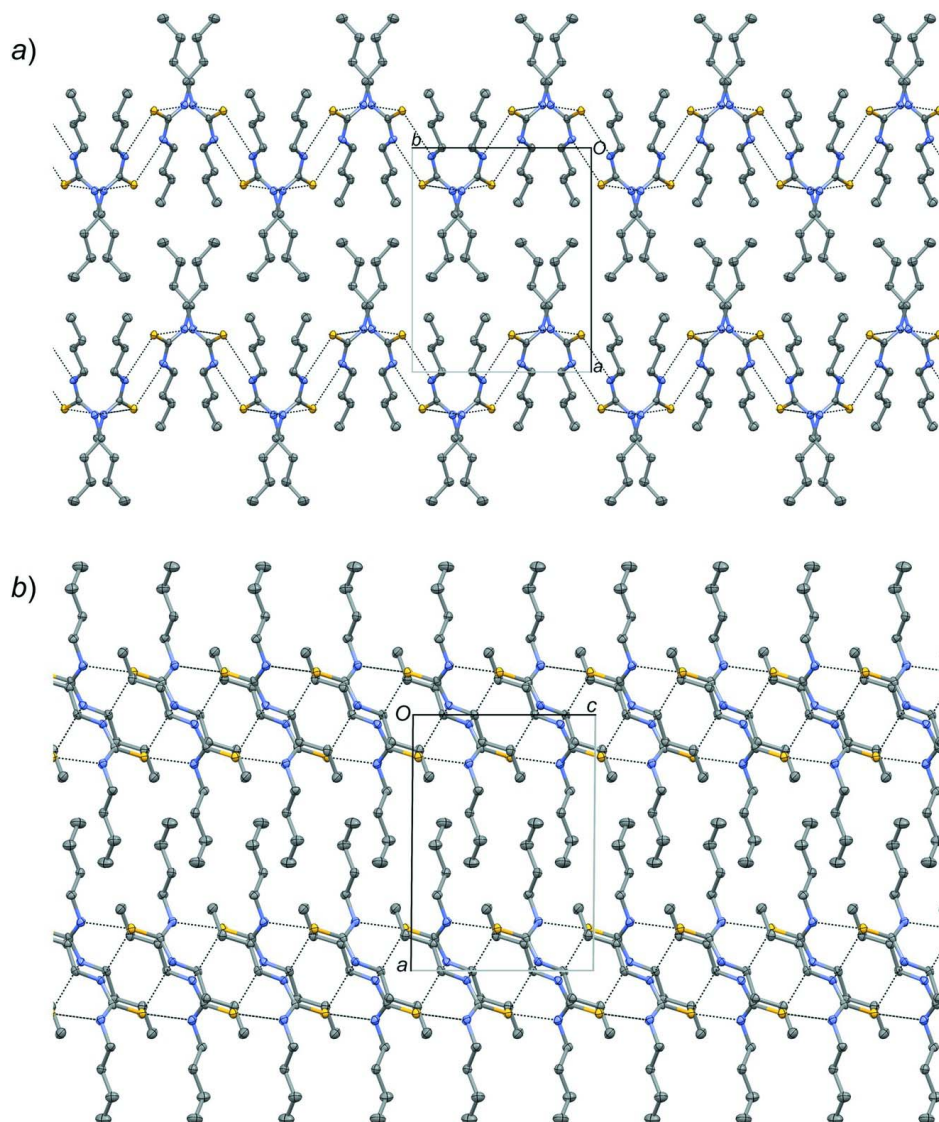
0.25 g (1.33 mmol) of commercially available *N,N'*-di-*n*-butylthiourea was dissolved in 2 ml of freshly distilled acetylacetone. The mixture was filtered and the filtrate was left for crystallization in a refrigerator. After several days well formed, colorless crystals were collected. Melting point: 335 - 337 K.

S3. Refinement

Hydrogen atoms were placed at the calculated positions ($d_{\text{CH}} = 0.98\text{--}0.99$ Å) and were treated as riding on their parent atoms, with $U_{\text{iso}}(\text{H})$ set to 1.2–1.5 times $U_{\text{eq}}(\text{C})$. The N—H distances were restrained to 0.85 (1) Å.

**Figure 1**

Structure of $[\text{SC}(\text{NH}^t\text{Bu})_2]_2$ dimer with the thermal ellipsoids drawn at 50% probability level. Hydrogen bonds marked with dotted lines. Symmetry code (i): $-x, -y + 1, -z + 2$.

**Figure 2**

Layers of $\text{SC}(\text{NH}^i\text{Bu})_2$ seen in the *a*) [001] and *b*) [010] direction. Hydrogen bonds marked with dotted lines, hydrogen atoms omitted for clarity.

1,3-Di-*n*-butylthiourea

Crystal data

$\text{C}_9\text{H}_{20}\text{N}_2\text{S}$

$M_r = 188.33$

Monoclinic, $P2_1/c$

Hall symbol: -P 2ybc

$a = 12.6395(6) \text{ \AA}$

$b = 10.0836(6) \text{ \AA}$

$c = 9.0128(5) \text{ \AA}$

$\beta = 90.476(5)^\circ$

$V = 1148.66(11) \text{ \AA}^3$

$Z = 4$

$F(000) = 416$

$D_x = 1.089 \text{ Mg m}^{-3}$

Melting point: 336(1) K

Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$

Cell parameters from 2942 reflections

$\theta = 2.6\text{--}28.6^\circ$

$\mu = 0.24 \text{ mm}^{-1}$

$T = 120 \text{ K}$

Prism, clear colourless

$0.48 \times 0.29 \times 0.09 \text{ mm}$

Data collection

Oxford Diffraction Xcalibur Sapphire2 diffractometer

Graphite monochromator

Detector resolution: 8.1883 pixels mm⁻¹

ω scans

Absorption correction: analytical
[*CrysAlis PRO* (Oxford Diffraction, 2010; based on Clark & Reid, 1995)]

$T_{\min} = 0.94$, $T_{\max} = 0.978$

5268 measured reflections

2247 independent reflections

1656 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.038$

$\theta_{\max} = 26^\circ$, $\theta_{\min} = 2.6^\circ$

$h = -15 \rightarrow 15$

$k = -12 \rightarrow 12$

$l = -10 \rightarrow 11$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.046$

$wR(F^2) = 0.116$

$S = 0.97$

2247 reflections

119 parameters

2 restraints

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0753P)^2]$

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

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

$\Delta\rho_{\max} = 0.45 \text{ e } \text{\AA}^{-3}$

$\Delta\rho_{\min} = -0.27 \text{ e } \text{\AA}^{-3}$

Special details

Experimental. *CrysAlisPro*, Oxford Diffraction Ltd., Version 1.171.33.66 (Oxford Diffraction, 2010) Analytical numeric absorption correction using a multifaceted crystal model based on expressions derived by Clark & Reid (1995).

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

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

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	0.16510 (4)	0.55610 (5)	1.03064 (5)	0.02246 (18)
N1	0.03660 (13)	0.60898 (18)	0.80521 (17)	0.0218 (4)
N2	0.19164 (13)	0.72585 (17)	0.80620 (18)	0.0229 (4)
C1	0.12922 (15)	0.63626 (19)	0.8705 (2)	0.0209 (4)
C2	-0.00052 (15)	0.6657 (2)	0.6656 (2)	0.0225 (5)
H2A	0.0525	0.649	0.5877	0.027*
H2B	-0.0082	0.7629	0.6769	0.027*
C3	-0.10604 (15)	0.6065 (2)	0.6181 (2)	0.0232 (5)
H3A	-0.1004	0.5086	0.6174	0.028*
H3B	-0.1608	0.6314	0.6909	0.028*
C4	-0.13954 (16)	0.6542 (2)	0.4653 (2)	0.0260 (5)
H4A	-0.0831	0.6327	0.3938	0.031*
H4B	-0.1475	0.7518	0.4676	0.031*

C5	-0.24282 (17)	0.5926 (2)	0.4116 (2)	0.0332 (5)
H5A	-0.2359	0.4959	0.4103	0.05*
H5B	-0.259	0.6244	0.3112	0.05*
H5C	-0.3001	0.618	0.4785	0.05*
C6	0.29696 (15)	0.7629 (2)	0.8598 (2)	0.0239 (5)
H6A	0.296	0.7677	0.9695	0.029*
H6B	0.3145	0.8523	0.8218	0.029*
C7	0.38310 (15)	0.6662 (2)	0.8128 (2)	0.0254 (5)
H7A	0.365	0.5764	0.8489	0.03*
H7B	0.3855	0.6629	0.7031	0.03*
C8	0.49139 (17)	0.7044 (2)	0.8722 (3)	0.0355 (6)
H8A	0.489	0.7081	0.9819	0.043*
H8B	0.5097	0.7941	0.8357	0.043*
C9	0.57675 (19)	0.6074 (3)	0.8255 (3)	0.0469 (7)
H9A	0.5583	0.5182	0.8596	0.07*
H9B	0.6446	0.634	0.8697	0.07*
H9C	0.5824	0.6075	0.7172	0.07*
H1	-0.0032 (14)	0.5586 (19)	0.854 (2)	0.028 (6)*
H2	0.1715 (15)	0.7675 (18)	0.7292 (15)	0.019 (6)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0254 (3)	0.0207 (3)	0.0213 (3)	0.0005 (2)	0.00074 (19)	0.0018 (2)
N1	0.0218 (9)	0.0250 (9)	0.0188 (8)	-0.0043 (8)	0.0011 (7)	0.0019 (7)
N2	0.0238 (9)	0.0227 (9)	0.0221 (9)	-0.0016 (7)	-0.0019 (7)	0.0047 (7)
C1	0.0251 (10)	0.0180 (10)	0.0197 (10)	0.0039 (8)	0.0051 (8)	-0.0024 (8)
C2	0.0257 (10)	0.0213 (11)	0.0206 (10)	0.0003 (9)	0.0037 (8)	0.0015 (8)
C3	0.0234 (10)	0.0223 (10)	0.0238 (11)	-0.0007 (8)	0.0013 (8)	0.0018 (8)
C4	0.0325 (12)	0.0223 (11)	0.0232 (11)	-0.0027 (9)	-0.0003 (9)	0.0014 (8)
C5	0.0325 (12)	0.0355 (13)	0.0313 (12)	-0.0036 (10)	-0.0068 (10)	0.0028 (10)
C6	0.0226 (10)	0.0219 (11)	0.0272 (11)	-0.0047 (9)	-0.0010 (8)	0.0011 (8)
C7	0.0251 (11)	0.0280 (11)	0.0230 (10)	0.0000 (9)	-0.0003 (8)	0.0020 (9)
C8	0.0276 (12)	0.0329 (13)	0.0460 (14)	-0.0016 (10)	-0.0010 (10)	0.0020 (11)
C9	0.0292 (13)	0.0475 (16)	0.0641 (18)	0.0056 (12)	0.0016 (12)	0.0049 (14)

Geometric parameters (Å, °)

S1—C1	1.712 (2)	C5—H5A	0.98
N1—C1	1.334 (2)	C5—H5B	0.98
N1—C2	1.456 (2)	C5—H5C	0.98
N1—H1	0.844 (9)	C6—C7	1.524 (3)
N2—C1	1.335 (3)	C6—H6A	0.99
N2—C6	1.461 (3)	C6—H6B	0.99
N2—H2	0.849 (9)	C7—C8	1.515 (3)
C2—C3	1.519 (3)	C7—H7A	0.99
C2—H2A	0.99	C7—H7B	0.99
C2—H2B	0.99	C8—C9	1.518 (3)

C3—C4	1.515 (3)	C8—H8A	0.99
C3—H3A	0.99	C8—H8B	0.99
C3—H3B	0.99	C9—H9A	0.98
C4—C5	1.521 (3)	C9—H9B	0.98
C4—H4A	0.99	C9—H9C	0.98
C4—H4B	0.99		
C1—N1—C2	125.10 (17)	H5A—C5—H5B	109.5
C1—N1—H1	114.7 (15)	C4—C5—H5C	109.5
C2—N1—H1	120.1 (15)	H5A—C5—H5C	109.5
C1—N2—C6	124.74 (17)	H5B—C5—H5C	109.5
C1—N2—H2	121.0 (14)	N2—C6—C7	113.32 (17)
C6—N2—H2	114.2 (14)	N2—C6—H6A	108.9
N1—C1—N2	117.90 (18)	C7—C6—H6A	108.9
N1—C1—S1	119.96 (15)	N2—C6—H6B	108.9
N2—C1—S1	122.13 (15)	C7—C6—H6B	108.9
N1—C2—C3	111.42 (16)	H6A—C6—H6B	107.7
N1—C2—H2A	109.3	C8—C7—C6	112.61 (18)
C3—C2—H2A	109.3	C8—C7—H7A	109.1
N1—C2—H2B	109.3	C6—C7—H7A	109.1
C3—C2—H2B	109.3	C8—C7—H7B	109.1
H2A—C2—H2B	108	C6—C7—H7B	109.1
C4—C3—C2	111.70 (16)	H7A—C7—H7B	107.8
C4—C3—H3A	109.3	C7—C8—C9	112.3 (2)
C2—C3—H3A	109.3	C7—C8—H8A	109.1
C4—C3—H3B	109.3	C9—C8—H8A	109.1
C2—C3—H3B	109.3	C7—C8—H8B	109.1
H3A—C3—H3B	107.9	C9—C8—H8B	109.1
C3—C4—C5	113.14 (17)	H8A—C8—H8B	107.9
C3—C4—H4A	109	C8—C9—H9A	109.5
C5—C4—H4A	109	C8—C9—H9B	109.5
C3—C4—H4B	109	H9A—C9—H9B	109.5
C5—C4—H4B	109	C8—C9—H9C	109.5
H4A—C4—H4B	107.8	H9A—C9—H9C	109.5
C4—C5—H5A	109.5	H9B—C9—H9C	109.5
C4—C5—H5B	109.5		
C2—N1—C1—N2	2.5 (3)	N1—C2—C3—C4	-173.97 (16)
C2—N1—C1—S1	-176.99 (15)	C2—C3—C4—C5	177.74 (17)
C6—N2—C1—N1	-177.36 (17)	C1—N2—C6—C7	81.5 (2)
C6—N2—C1—S1	2.1 (3)	N2—C6—C7—C8	-178.71 (17)
C1—N1—C2—C3	176.27 (17)	C6—C7—C8—C9	179.74 (19)

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1 \cdots S1 ⁱ	0.84 (1)	2.58 (1)	3.3943 (17)	164 (2)



N2—H2...S1 ⁱⁱ	0.85 (1)	2.52 (1)	3.3319 (17)	159 (2)
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Symmetry codes: (i) $-x, -y+1, -z+2$; (ii) $x, -y+3/2, z-1/2$.