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1,3-Bis(2-chlorophenyl)thiourea: a monoclinic polymorph

Chien Ing Yeo and Edward R. T. Tiekink*

 Department of Chemistry, University of Malaya, 50603 Kuala Lumpur, Malaysia
 Correspondence e-mail: edward.tiekink@gmail.com

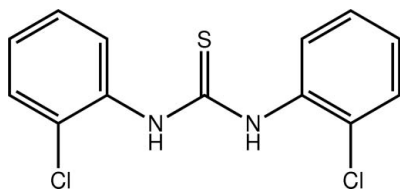
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 Key indicators: single-crystal X-ray study; $T = 100$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å; R factor = 0.038; wR factor = 0.090; data-to-parameter ratio = 18.3.

The title compound, $\text{C}_{13}\text{H}_{10}\text{Cl}_2\text{N}_2\text{S}$, represents a monoclinic polymorph of the previously reported orthorhombic form [Ramnathan *et al.* (1996). *Acta Cryst.* **C52**, 134–136]. The molecule is twisted with the dihedral angle between the benzene rings being $55.37(7)^\circ$. The N–H atoms are *syn* to each other, which contrasts their *anti* disposition in the orthorhombic form. In the crystal, molecules assemble into zigzag chains along the *c* axis via N–H \cdots S hydrogen bonds. Chains are connected into layers via C–H \cdots Cl interactions, and these stack along the *a* axis.

Related literature

For background to the structural chemistry of thiocarbamides, see: Ho *et al.* (2005). For a related diarylthiourea structure, see: Kuan & Tiekink (2007). For the structure of the orthorhombic polymorph, see: Ramnathan *et al.* (1996).



Experimental

Crystal data

$\text{C}_{13}\text{H}_{10}\text{Cl}_2\text{N}_2\text{S}$
 $M_r = 297.19$
 Monoclinic, $P2_1/c$
 $a = 11.9999(3)$ Å

$b = 14.6811(3)$ Å
 $c = 8.0806(2)$ Å
 $\beta = 109.509(1)^\circ$
 $V = 1341.84(5)$ Å³

$Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 0.62$ mm⁻¹

$T = 100$ K
 $0.20 \times 0.06 \times 0.02$ mm

Data collection

Bruker SMART APEX
 diffractometer
 Absorption correction: multi-scan
 (SADABS; Sheldrick, 1996)
 $T_{\min} = 0.644$, $T_{\max} = 0.746$

12491 measured reflections
 3090 independent reflections
 2291 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.052$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.038$
 $wR(F^2) = 0.090$
 $S = 1.02$
 3090 reflections
 169 parameters
 2 restraints

H atoms treated by a mixture of
 independent and constrained
 refinement
 $\Delta\rho_{\text{max}} = 0.35$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.43$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1–H1n \cdots S1 ⁱ	0.87 (2)	2.62 (2)	3.4449 (18)	159 (2)
N2–H2n \cdots S1 ⁱ	0.87 (2)	2.49 (2)	3.3389 (18)	166 (2)
C13–H13 \cdots Cl2 ⁱⁱ	0.95	2.79	3.660 (2)	152

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

Data collection: APEX2 (Bruker, 2009); cell refinement: SAINT (Bruker, 2009); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: ORTEP-3 (Farrugia, 1997), DIAMOND (Brandenburg, 2006) and Qmol (Gans & Shalloway, 2001); software used to prepare material for publication: publCIF (Westrip, 2010).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: VM2125).

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supporting information

Acta Cryst. (2011). E67, o2965 [doi:10.1107/S1600536811041894]

1,3-Bis(2-chlorophenyl)thiourea: a monoclinic polymorph

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S1. Comment

In connection with the synthesis and structural studies of thiocarbamides (Ho *et al.*, 2005), diarylthioureas are sometimes isolated as the undesired hydrolysis by-product (Kuan & Tiekink, 2007). The title compound, (I), was isolated in crystalline form during the attempted synthesis of (C₆H₄Cl-*o*)N(H)C(=S)O-*i*-Pr. The structure of (I) is reported herein. A previously reported orthorhombic form of (I) exists in the literature (Ramnathan *et al.*, 1996).

The molecular structure of (I), Fig. 1, is twisted about the central N—C bonds. With reference to the central plane through the CN₂S chromophore [r.m.s. deviation = 0.0029 Å], the C2-benzene ring is almost perpendicular [dihedral angle = 85.20 (6)°] and the C8-ring is twisted [dihedral angle = 49.32 (6)°]; the dihedral angle between the benzene rings is 55.37 (7)°. The amide-H atoms are *syn* to each other. The *syn* conformation observed for the thiourea chromophore in (I) is quite distinct to that found in the orthorhombic polymorph (Ramnathan *et al.*, 1996).

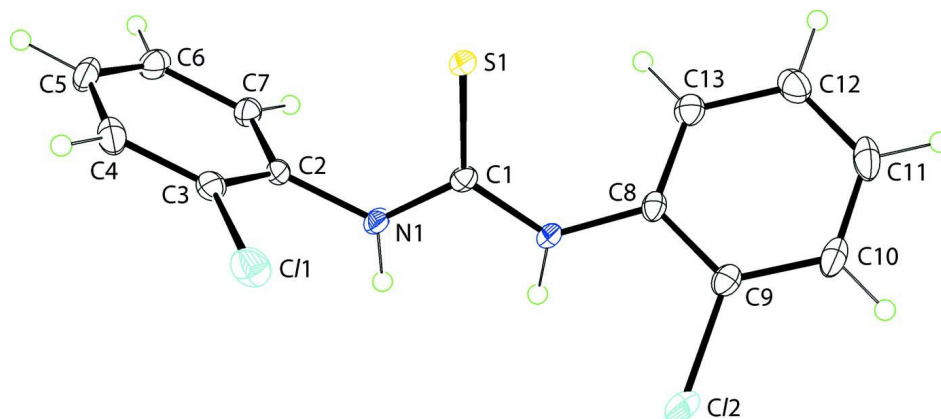
In the orthorhombic form of (I), the amide-H atoms are *anti* to each other. This key difference between the molecular structures in the two polymorphs is highlighted in the overlay diagram shown in Fig. 2. The *anti* orientation allows for the formation of eight-membered {···HNCS}₂ synthons in the crystal packing in the orthorhombic polymorph. By contrast, the crystal structure of (I) features supramolecular zigzag chains along the *c* axis mediated by N—H···S hydrogen bonds (Table 1 and Fig. 3); the S1 atom is bifurcated. Chains assemble into layers by C—H···Cl interactions (Fig. 4) and the layers thus formed stack along the *a* axis (Fig. 5).

S2. Experimental

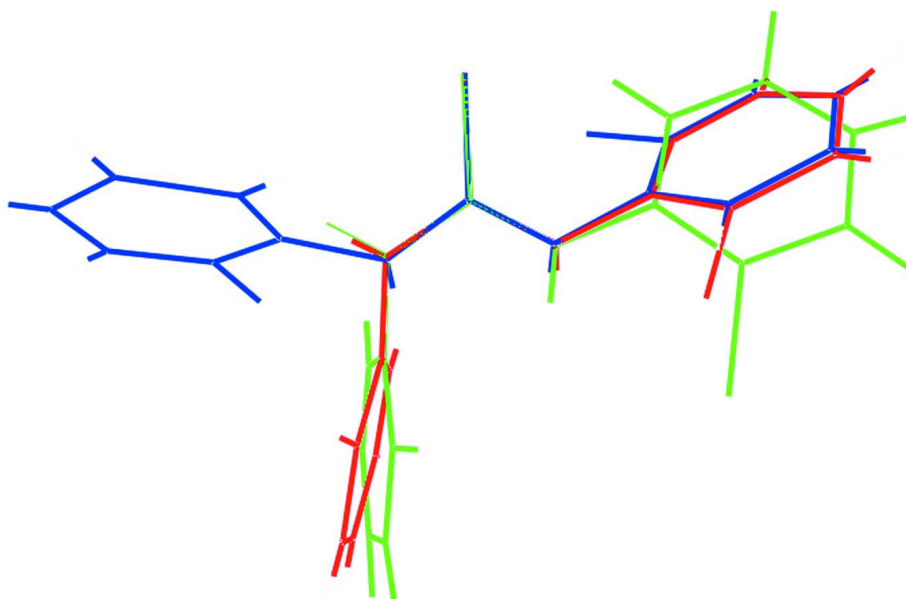
2-Chlorophenyl isothiocyanate (2 ml) was added drop-wise to a stirred solution of NaOH (1 mol equiv.) in *i*-PrOH (25 ml) and stirred for 3 h. Excess HCl (50% *M/v*) was then added and the solution was stirred for a further 2 h. The product was then extracted with CHCl₃ and left for evaporation at room temperature yielding colourless crystals after 3 days; *M.pt.*: 394–396 K. IR (cm⁻¹): ν(N—H) 3348; ν(C—N) 1498; ν(C=S) 1201.

S3. Refinement

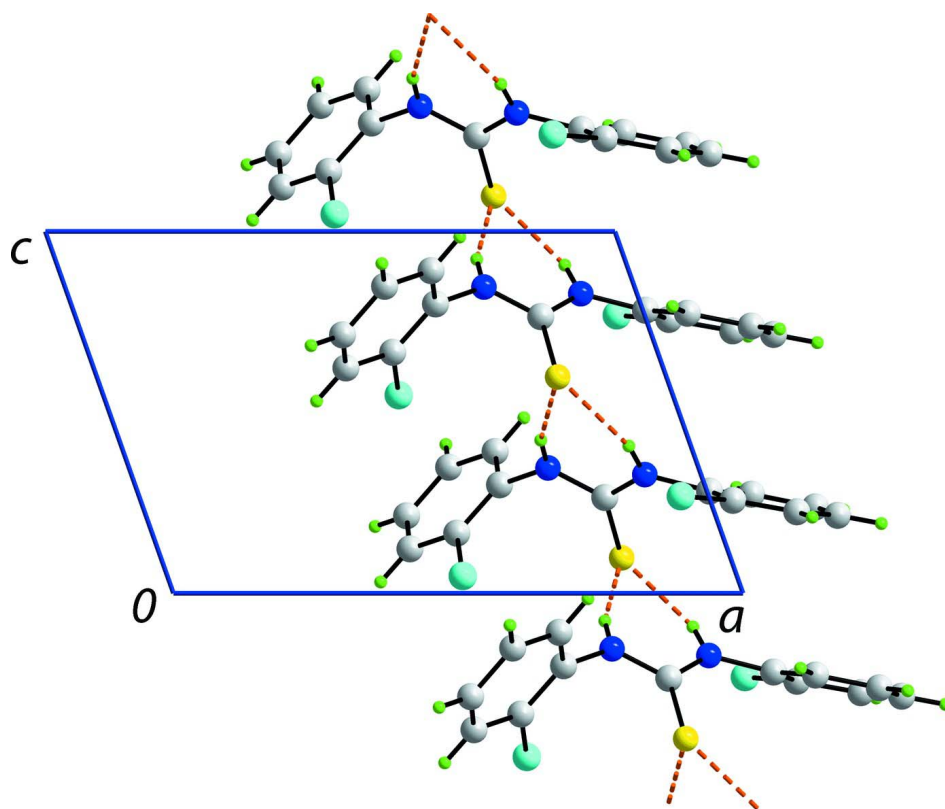
Carbon-bound H-atoms were placed in calculated positions (C—H 0.95 Å) and were included in the refinement in the riding model approximation, with $U_{\text{iso}}(\text{H})$ set to $1.2U_{\text{eq}}(\text{C})$. The N-bound H-atoms were located in a difference Fourier map but were refined with a distance restraint of N—H = 0.88±0.01 Å, and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{N})$.

**Figure 1**

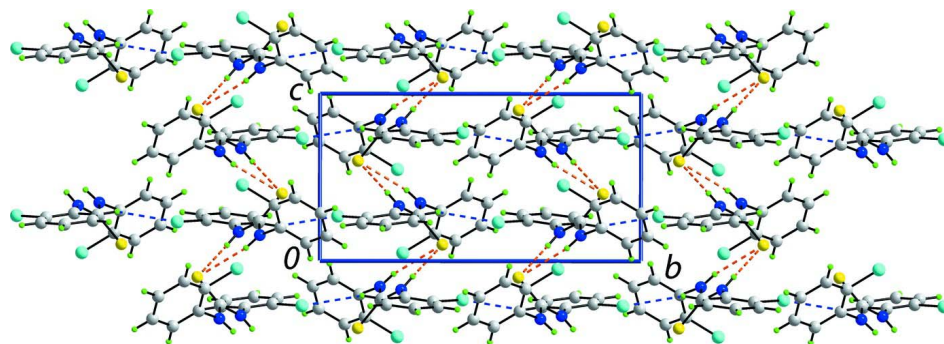
The molecular structure of (I) showing the atom-labelling scheme and displacement ellipsoids at the 50% probability level.

**Figure 2**

Overlay diagram of (I) (shown in blue) with the two independent molecules found in the orthorhombic polymorph (see text), shown in red and green. The central thiourea fragments have been fitted.

**Figure 3**

Supramolecular zigzag chain in (I) mediated by N—H...S hydrogen bonds, shown as orange dashed lines.

**Figure 4**

A view of the supramolecular two-dimensional array in the bc plane for (I). The N—H...S and C—H...Cl contacts are shown as orange and blue dashed lines, respectively.

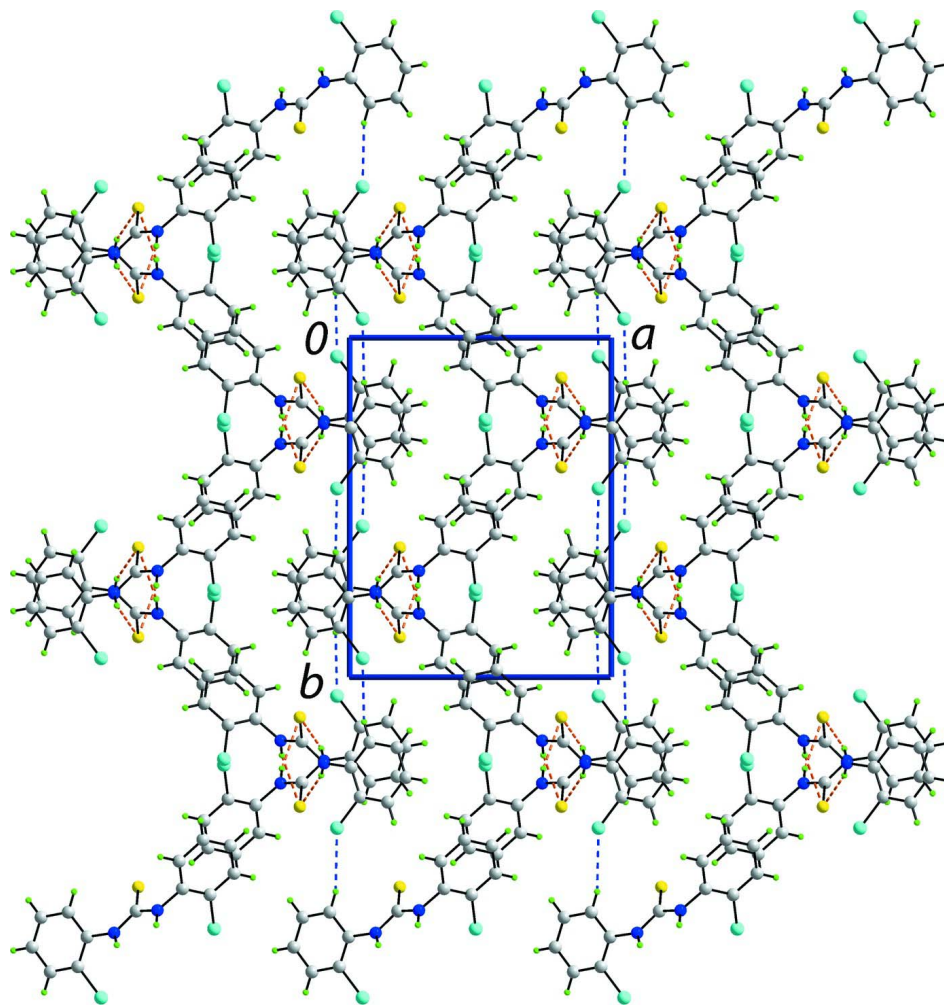


Figure 5

Unit-cell contents for (I) shown in projection down the c axis, showing the stacking of supramolecular layers along the a axis. The N—H...S and C—H...Cl contacts are shown as orange and blue dashed lines, respectively.

1,3-Bis(2-chlorophenyl)thiourea

Crystal data

$C_{13}H_{10}Cl_2N_2S$

$M_r = 297.19$

Monoclinic, $P2_1/c$

Hall symbol: $-P\ 2_1/c$

$a = 11.9999\ (3)\ \text{\AA}$

$b = 14.6811\ (3)\ \text{\AA}$

$c = 8.0806\ (2)\ \text{\AA}$

$\beta = 109.509\ (1)^\circ$

$V = 1341.84\ (5)\ \text{\AA}^3$

$Z = 4$

$F(000) = 608$

$D_x = 1.471\ \text{Mg m}^{-3}$

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

Cell parameters from 2105 reflections

$\theta = 2.3\text{--}25.4^\circ$

$\mu = 0.62\ \text{mm}^{-1}$

$T = 100\ \text{K}$

Prism, colourless

$0.20 \times 0.06 \times 0.02\ \text{mm}$

Data collection

Bruker SMART APEX
diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
 ω scans
Absorption correction: multi-scan
(*SADABS*; Sheldrick, 1996)
 $T_{\min} = 0.644$, $T_{\max} = 0.746$

12491 measured reflections
3090 independent reflections
2291 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.052$
 $\theta_{\text{max}} = 27.5^\circ$, $\theta_{\text{min}} = 2.3^\circ$
 $h = -15 \rightarrow 15$
 $k = -19 \rightarrow 19$
 $l = -10 \rightarrow 10$

Refinement

Refinement on F^2
Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.038$
 $wR(F^2) = 0.090$
 $S = 1.02$
3090 reflections
169 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
 $w = 1/[\sigma^2(F_o^2) + (0.0375P)^2 + 0.4482P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.35 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.43 \text{ e } \text{\AA}^{-3}$

Special details

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>	$U_{\text{iso}}^*/U_{\text{eq}}$
Cl2	0.95110 (5)	0.44450 (4)	0.76829 (8)	0.03177 (16)
Cl1	0.51862 (5)	0.24151 (4)	0.54764 (9)	0.03412 (17)
S1	0.80893 (5)	0.11833 (4)	0.59792 (7)	0.01789 (13)
N1	0.73545 (16)	0.18714 (12)	0.8464 (2)	0.0200 (4)
H1N	0.740 (2)	0.2301 (12)	0.923 (2)	0.024*
N2	0.90127 (15)	0.25343 (12)	0.8279 (2)	0.0189 (4)
H2N	0.891 (2)	0.2893 (13)	0.907 (2)	0.023*
C1	0.81669 (17)	0.18925 (14)	0.7647 (3)	0.0171 (4)
C2	0.63988 (18)	0.12309 (15)	0.7997 (3)	0.0192 (4)
C3	0.53473 (19)	0.14084 (15)	0.6660 (3)	0.0223 (5)
C4	0.4428 (2)	0.07777 (17)	0.6227 (3)	0.0280 (5)
H4	0.3708	0.0904	0.5311	0.034*
C5	0.4575 (2)	-0.00316 (17)	0.7142 (3)	0.0290 (6)
H5	0.3955	-0.0468	0.6845	0.035*
C6	0.5615 (2)	-0.02114 (16)	0.8484 (3)	0.0274 (5)

H6	0.5708	-0.0769	0.9112	0.033*
C7	0.6528 (2)	0.04214 (15)	0.8918 (3)	0.0223 (5)
H7	0.7242	0.0298	0.9849	0.027*
C8	1.00456 (18)	0.26531 (15)	0.7822 (3)	0.0190 (5)
C9	1.03988 (19)	0.35296 (15)	0.7568 (3)	0.0227 (5)
C10	1.1449 (2)	0.36828 (17)	0.7252 (3)	0.0292 (6)
H10	1.1687	0.4286	0.7104	0.035*
C11	1.2144 (2)	0.2954 (2)	0.7154 (3)	0.0340 (6)
H11	1.2861	0.3054	0.6927	0.041*
C12	1.1804 (2)	0.20762 (18)	0.7386 (3)	0.0308 (6)
H12	1.2284	0.1575	0.7303	0.037*
C13	1.07637 (19)	0.19243 (16)	0.7739 (3)	0.0248 (5)
H13	1.0543	0.1321	0.7925	0.030*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C12	0.0352 (3)	0.0165 (3)	0.0443 (4)	-0.0053 (2)	0.0142 (3)	0.0001 (3)
C11	0.0332 (3)	0.0314 (3)	0.0386 (4)	0.0093 (3)	0.0131 (3)	0.0113 (3)
S1	0.0192 (3)	0.0152 (3)	0.0199 (3)	-0.0022 (2)	0.0072 (2)	-0.0024 (2)
N1	0.0229 (9)	0.0184 (9)	0.0211 (10)	-0.0073 (8)	0.0105 (8)	-0.0070 (8)
N2	0.0195 (9)	0.0151 (9)	0.0231 (10)	-0.0049 (7)	0.0083 (8)	-0.0045 (7)
C1	0.0179 (10)	0.0135 (10)	0.0179 (11)	0.0006 (8)	0.0034 (8)	0.0024 (8)
C2	0.0181 (10)	0.0202 (11)	0.0229 (11)	-0.0039 (9)	0.0115 (9)	-0.0062 (9)
C3	0.0243 (12)	0.0221 (12)	0.0242 (12)	-0.0004 (9)	0.0130 (9)	-0.0013 (9)
C4	0.0197 (11)	0.0412 (15)	0.0239 (12)	-0.0041 (10)	0.0083 (9)	-0.0069 (11)
C5	0.0287 (13)	0.0330 (14)	0.0307 (13)	-0.0163 (11)	0.0170 (11)	-0.0129 (11)
C6	0.0358 (13)	0.0212 (12)	0.0312 (13)	-0.0065 (10)	0.0193 (11)	-0.0015 (10)
C7	0.0228 (11)	0.0225 (11)	0.0232 (12)	-0.0032 (9)	0.0099 (9)	-0.0019 (9)
C8	0.0161 (10)	0.0221 (11)	0.0176 (11)	-0.0049 (9)	0.0041 (8)	-0.0021 (9)
C9	0.0234 (11)	0.0225 (11)	0.0206 (11)	-0.0055 (9)	0.0051 (9)	-0.0026 (9)
C10	0.0287 (13)	0.0324 (14)	0.0274 (13)	-0.0157 (11)	0.0104 (10)	-0.0035 (11)
C11	0.0210 (12)	0.0528 (17)	0.0298 (14)	-0.0131 (12)	0.0108 (10)	-0.0079 (12)
C12	0.0210 (12)	0.0378 (14)	0.0325 (14)	0.0013 (11)	0.0075 (10)	-0.0076 (11)
C13	0.0202 (11)	0.0252 (12)	0.0261 (12)	-0.0016 (10)	0.0037 (9)	-0.0023 (10)

Geometric parameters (Å, °)

C12—C9	1.737 (2)	C5—H5	0.9500
C11—C3	1.736 (2)	C6—C7	1.389 (3)
S1—C1	1.681 (2)	C6—H6	0.9500
N1—C1	1.348 (3)	C7—H7	0.9500
N1—C2	1.433 (3)	C8—C9	1.391 (3)
N1—H1N	0.871 (10)	C8—C13	1.389 (3)
N2—C1	1.354 (3)	C9—C10	1.385 (3)
N2—C8	1.417 (3)	C10—C11	1.375 (4)
N2—H2N	0.872 (9)	C10—H10	0.9500
C2—C7	1.383 (3)	C11—C12	1.383 (4)

C2—C3	1.384 (3)	C11—H11	0.9500
C3—C4	1.392 (3)	C12—C13	1.388 (3)
C4—C5	1.379 (3)	C12—H12	0.9500
C4—H4	0.9500	C13—H13	0.9500
C5—C6	1.379 (3)		
C1—N1—C2	122.16 (18)	C7—C6—H6	120.0
C1—N1—H1N	116.2 (16)	C2—C7—C6	120.1 (2)
C2—N1—H1N	121.4 (16)	C2—C7—H7	120.0
C1—N2—C8	126.73 (18)	C6—C7—H7	120.0
C1—N2—H2N	115.1 (15)	C9—C8—C13	118.7 (2)
C8—N2—H2N	118.1 (15)	C9—C8—N2	119.22 (19)
N1—C1—N2	113.90 (18)	C13—C8—N2	121.9 (2)
N1—C1—S1	121.53 (16)	C10—C9—C8	121.2 (2)
N2—C1—S1	124.56 (16)	C10—C9—C12	119.76 (18)
C7—C2—C3	119.4 (2)	C8—C9—C12	119.03 (17)
C7—C2—N1	119.08 (19)	C11—C10—C9	119.4 (2)
C3—C2—N1	121.5 (2)	C11—C10—H10	120.3
C2—C3—C4	120.7 (2)	C9—C10—H10	120.3
C2—C3—C11	119.68 (17)	C10—C11—C12	120.4 (2)
C4—C3—C11	119.65 (18)	C10—C11—H11	119.8
C5—C4—C3	119.3 (2)	C12—C11—H11	119.8
C5—C4—H4	120.3	C11—C12—C13	120.2 (2)
C3—C4—H4	120.3	C11—C12—H12	119.9
C4—C5—C6	120.4 (2)	C13—C12—H12	119.9
C4—C5—H5	119.8	C12—C13—C8	120.1 (2)
C6—C5—H5	119.8	C12—C13—H13	120.0
C5—C6—C7	120.1 (2)	C8—C13—H13	120.0
C5—C6—H6	120.0		

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>
N1—H1n \cdots S1 ⁱ	0.87 (2)	2.62 (2)	3.4449 (18)	159 (2)
N2—H2n \cdots S1 ⁱ	0.87 (2)	2.49 (2)	3.3389 (18)	166 (2)
C13—H13 \cdots C12 ⁱⁱ	0.95	2.79	3.660 (2)	152

Symmetry codes: (i) $x, -y+1/2, z+1/2$; (ii) $-x+2, y-1/2, -z+3/2$.