organic compounds

(2E)-2-[2-(Cyclohexylcarbamothioyl)-hydrazinylidene]propanoic acid

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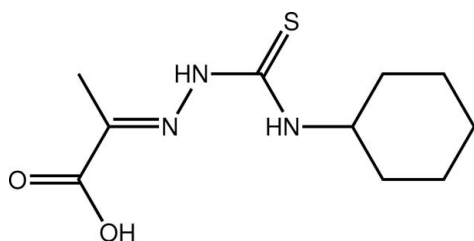Correspondence e-mail: edward.tiekink@gmail.com

In the title thiourea derivative, $C_{10}H_{17}N_3O_2S$, the carboxyl group and the least-squares plane through the cyclohexyl ring are twisted out of the plane through the central CN_3S residue; the respective dihedral angles are 7.18 (8) and 62.29 (4)°. The conformation about the azomethine bond [1.275 (2) Å] is E. The NH groups are *anti*, with one forming an intramolecular N—H⋯N hydrogen bond. The main feature of the crystal structure is the formation of linear supramolecular chains along [110] mediated by alternating pairs of O—H⋯O and pairs of N—H⋯S hydrogen bonds.

Related literature

For related thiourea structures, see: Normaya *et al.* (2011); Salam *et al.* (2011).

Experimental

Crystal data

$C_{10}H_{17}N_3O_2S$	V = 1209.93 (6) Å^3
M_r = 243.33	Z = 4
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation
a = 8.9204 (2) Å	μ = 0.26 mm^{-1}
b = 6.0350 (2) Å	T = 100 K
c = 22.4750 (6) Å	0.30 × 0.20 × 0.10 mm
β = 90.051 (3)°	

Data collection

Agilent Supernova Dual diffractometer with an Atlas detector	7394 measured reflections
	2723 independent reflections
Absorption correction: multi-scan (*CrysAlis PRO*; Agilent, 2010)	2251 reflections with $I > 2\sigma(I)$
	R_{int} = 0.036
T_{min} = 0.687, T_{max} = 1.000	

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.041	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2)$ = 0.143	
S = 0.98	
2723 reflections	$\Delta\rho_{max}$ = 0.36 e Å^{-3}
158 parameters	$\Delta\rho_{min}$ = −0.32 e Å^{-3}
3 restraints	

Table 1
Hydrogen-bond geometry (Å, °).

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
N3—H3⋯N1	0.87 (1)	2.20 (2)	2.574 (2)	106 (2)
O1—H1⋯O2^i	0.85 (1)	1.80 (1)	2.6416 (17)	172 (3)
N2—H2⋯S1^{ii}	0.89 (1)	2.65 (1)	3.5384 (15)	176 (2)

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

Data collection: *CrysAlis PRO* (Agilent, 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: *ORTEP-3* (Farrugia, 1997) and *DIAMOND* (Brandenburg, 2006); software used to prepare material for publication: *publCIF* (Westrip, 2010).

References

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supporting information

(2*E*)-2-[2-(Cyclohexylcarbamothioyl)hydrazinylidene]propanoic acid

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S1. Comment

In continuation of structural investigations into conformation and hydrogen bonding in thiourea derivatives (Normaya *et al.* 2011; Salam *et al.*, 2011), the title compound, (I), was investigated.

The central CN$_3$S chromophore in (I), Fig. 1, is planar (r.m.s. = 0.0039 Å). The carboxylate residue is slightly twisted out this plane (dihedral angle = 7.18 (8) °), and, by contrast, the least-squares plane through the cyclohexyl group (which has the conformation of a chair) is twisted significantly out of the central plane (dihedral angle = 62.29 (4) °). The H atoms of the NH groups are *anti*, and the conformation about the azomethine bond [1.275 (2) Å] is *E*. The N3—H forms an intramolecular hydrogen bond with the imino-N3 atom, Table 1. Finally, the thione and carboxylic acid groups lie to opposite sides of the molecule. This arrangements enables the formation of linear supramolecular chains *via* hydrogen bonds along [110] in the crystal packing, Fig. 2 and Table 1. The carboxylic acid residues self-associate *via* a centrosymmetric eight-membered {···HOC═O}$_2$ synthon. Similarly, the thiourea entity with the NH atom not involved in the intramolecular N—H···N interaction, self-associates *via* a centrosymmetric eight-membered {···HNC═S}$_2$ synthon. Chains lie in the *ab* plane with the cyclohexyl rings inter-digitating along the *c* axis, Fig. 3.

S2. Experimental

Cyclohexylisothiocyanate (0.706 g, 5 mmol) and hydrazine hydrate (0.250 g, 5 mmol), each dissolved in 10 ml e thanol were mixed with constant stirring. The stirring was continued for 30 min and the white product that formed, *N*(4)-cyclo-hexylthiosemicarbazide, was washed with ethanol and dried *in vacuo*. A solution of this (0.51 g, 3 mmol) in 10 ml me thanol was refluxed with a methanolic solution of pyruvic acid (0.261 g, 3 mmol) for 5 h after the addition of 1–2 drops of glacial acetic acid. On cooling the solution to room temperature, white precipitate separated, which were filtered and washed with methanol. The white precipitate was recrystallized from methanol to yield colourless prisms and dried *in vacuo* over silica gel. (*M*.pt. 465–467 K. Yield 0.621 g (80%). Anal. Found: C, 49.31; H, 7.01; N, 17.18%. C$_{10}$H$_{17}$N$_3$O$_2$S requires: C, 49.36; H, 7.04; N, 17.26%. FT—IR (KBr, cm^{-1}) ν_{max}: 3322 (m, OH), 3197 (s, NH), 2922, 2851 (s, cyclo-hexyl), 1692 (m, C═O), 1619 (w, C═N), 980 (m, N—N), 1249, 873 (w, C═S).

S3. Refinement

Carbon-bound H-atoms were placed in calculated positions (C–H = 0.98 to 1.00 Å) and were included in the refinement in the riding model approximation, with U_{iso}(H) set to 1.2–1.5U_{eq}(C). The O– and N-bound H-atoms were located in a difference Fourier map and were refined with distance restraints of O—H = 0.84±0.01 Å and N—H 0.88±0.01 Å, and with U_{iso}(H) = yU_{eq}(N) for y = 1.5 (O) and 1.2 (N).
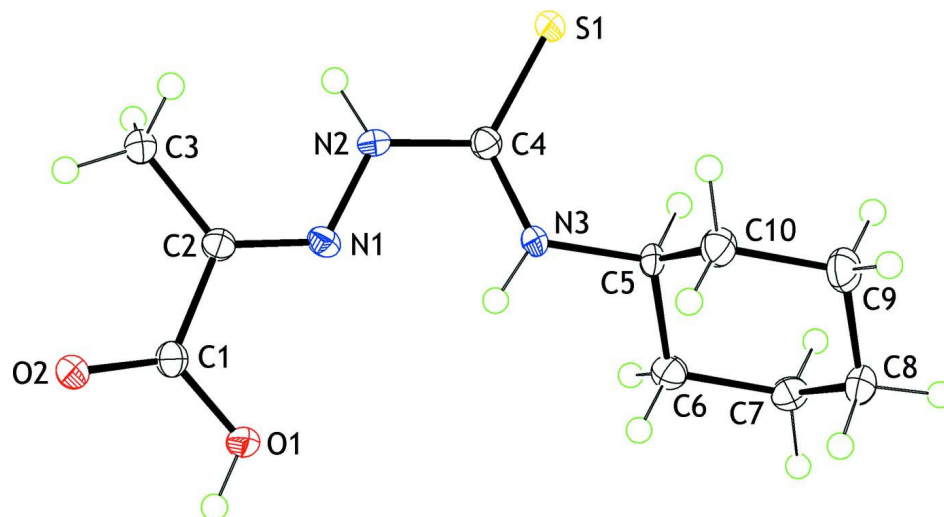
Figure 1

The molecular structure of (I) showing displacement ellipsoids at the 50% probability level.
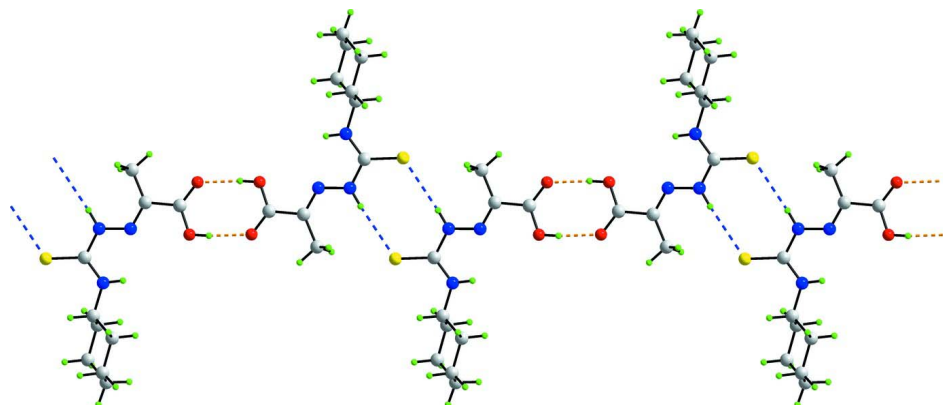
Figure 2

A view of the supramolecular chain aligned along [110] in (I). The O—H···O and N—H···S hydrogen bonds are shown as orange and blue dashed lines, respectively.
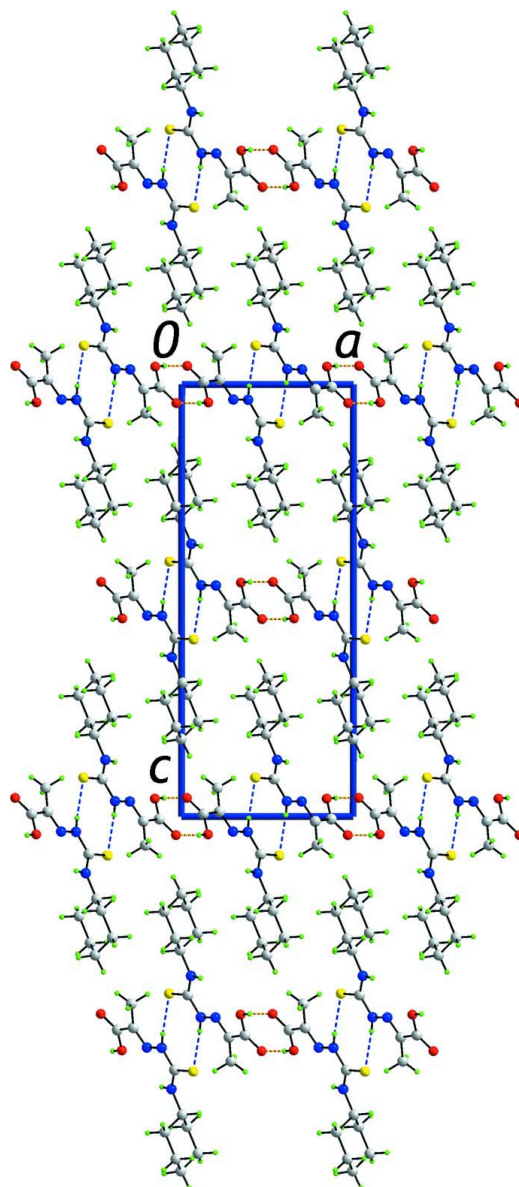
Figure 3

A view in projection down the *b* axis of the crystal packing in (I) showing the inter-digitation of the cyclohexyl rings along the *c* direction. The O—H···O and N—H···S hydrogen bonds are shown as orange and blue dashed lines, respectively.

(2*E*)-2-[2-(Cyclohexylcarbamothioyl)hydrazinylidene]propanoic acid

Crystal data

$C_{10}H_{17}N_3O_2S$	$\beta = 90.051\,(3)°$
$M_r = 243.33$	$V = 1209.93\,(6)$ Å^3
Monoclinic, $P2_1/n$	$Z = 4$
Hall symbol: -P 2yn	$F(000) = 520$
$a = 8.9204\,(2)$ Å	$D_x = 1.336$ Mg m^{-3}
$b = 6.0350\,(2)$ Å	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$c = 22.4750\,(6)$ Å	Cell parameters from 3312 reflections

$\theta = 2.3$–$29.1°$

$\mu = 0.26$ mm^{-1}

$T = 100$ K

Prism, colourless

$0.30 \times 0.20 \times 0.10$ mm

Data collection

Agilent Supernova Dual diffractometer with an Atlas detector	$T_{min} = 0.687$, $T_{max} = 1.000$
Radiation source: SuperNova (Mo) X-ray Source	7394 measured reflections
	2723 independent reflections
Mirror monochromator	2251 reflections with $I > 2\sigma(I)$
Detector resolution: 10.4041 pixels mm^{-1}	$R_{int} = 0.036$
ω scans	$\theta_{max} = 27.5°$, $\theta_{min} = 2.5°$
Absorption correction: multi-scan (*CrysAlis PRO*; Agilent, 2010)	$h = -11\rightarrow11$
	$k = -6\rightarrow7$
	$l = -29\rightarrow29$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.041$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.143$	
$S = 0.98$	H atoms treated by a mixture of independent and constrained refinement
2723 reflections	
158 parameters	$w = 1/[\sigma^2(F_o^2) + (0.1P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
3 restraints	
Primary atom site location: structure-invariant direct methods	$(\Delta/\sigma)_{max} = 0.001$
	$\Delta\rho_{max} = 0.36$ e Å^{-3}
	$\Delta\rho_{min} = -0.32$ e Å^{-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.

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 $F^2 > \sigma(F^2)$ 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 (Å^2)

	x	y	z	U_{iso}*/U_{eq}
S1	1.07001 (5)	1.46426 (7)	0.59008 (2)	0.01940 (18)
O1	0.65476 (14)	0.6300 (2)	0.54143 (6)	0.0209 (3)
O2	0.53180 (13)	0.7099 (2)	0.45694 (6)	0.0196 (3)
N1	0.80028 (16)	1.0010 (2)	0.53480 (7)	0.0156 (3)
N2	0.88614 (16)	1.1878 (2)	0.53543 (7)	0.0170 (3)
N3	0.94326 (16)	1.0938 (3)	0.63114 (7)	0.0169 (3)
C1	0.62814 (18)	0.7522 (3)	0.49413 (8)	0.0164 (4)
C2	0.72145 (19)	0.9564 (3)	0.48899 (8)	0.0162 (4)
C3	0.7098 (2)	1.0904 (3)	0.43363 (8)	0.0211 (4)
H3A	0.6904	1.2455	0.4440	0.032*
H3B	0.6273	1.0339	0.4091	0.032*
H3C	0.8039	1.0800	0.4113	0.032*

C4	0.96146 (18)	1.2376 (3)	0.58689 (8)	0.0156 (4)
C5	1.00682 (18)	1.1176 (3)	0.69060 (7)	0.0157 (4)
H5	1.1055	1.1951	0.6871	0.019*
C6	1.0336 (2)	0.8900 (3)	0.71759 (9)	0.0210 (4)
H6A	1.1037	0.8054	0.6921	0.025*
H6B	0.9377	0.8076	0.7194	0.025*
C7	1.0991 (2)	0.9113 (3)	0.78024 (8)	0.0221 (4)
H7A	1.1116	0.7618	0.7977	0.026*
H7B	1.1994	0.9811	0.7779	0.026*
C8	0.9984 (2)	1.0501 (3)	0.82063 (9)	0.0235 (4)
H8A	0.9019	0.9725	0.8267	0.028*
H8B	1.0471	1.0689	0.8599	0.028*
C9	0.9696 (2)	1.2771 (3)	0.79289 (9)	0.0250 (4)
H9A	0.8988	1.3610	0.8182	0.030*
H9B	1.0648	1.3611	0.7912	0.030*
C10	0.9048 (2)	1.2561 (3)	0.73033 (8)	0.0212 (4)
H10A	0.8046	1.1858	0.7325	0.025*
H10B	0.8924	1.4055	0.7128	0.025*
H1	0.602 (2)	0.514 (3)	0.5431 (12)	0.040 (7)*
H2	0.892 (2)	1.275 (3)	0.5035 (6)	0.026 (6)*
H3	0.888 (2)	0.976 (2)	0.6260 (11)	0.029 (6)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0251 (3)	0.0177 (3)	0.0154 (3)	−0.00825 (16)	−0.0030 (2)	0.00088 (18)
O1	0.0233 (6)	0.0208 (7)	0.0185 (7)	−0.0089 (5)	−0.0048 (5)	0.0055 (6)
O2	0.0200 (6)	0.0205 (7)	0.0182 (7)	−0.0064 (5)	−0.0030 (5)	0.0018 (5)
N1	0.0148 (7)	0.0144 (7)	0.0178 (8)	−0.0030 (5)	0.0009 (6)	−0.0010 (6)
N2	0.0214 (7)	0.0140 (7)	0.0157 (8)	−0.0039 (6)	−0.0007 (6)	0.0036 (6)
N3	0.0196 (7)	0.0172 (7)	0.0140 (8)	−0.0068 (6)	−0.0047 (6)	0.0006 (6)
C1	0.0159 (8)	0.0178 (9)	0.0155 (9)	0.0010 (7)	0.0000 (7)	−0.0017 (7)
C2	0.0153 (8)	0.0168 (9)	0.0166 (9)	−0.0015 (6)	0.0005 (7)	0.0006 (7)
C3	0.0247 (9)	0.0215 (9)	0.0169 (9)	−0.0069 (7)	−0.0040 (7)	0.0022 (8)
C4	0.0154 (8)	0.0160 (8)	0.0155 (8)	−0.0002 (6)	0.0004 (7)	−0.0008 (7)
C5	0.0173 (8)	0.0184 (9)	0.0112 (8)	−0.0030 (7)	−0.0038 (6)	−0.0006 (7)
C6	0.0255 (9)	0.0168 (9)	0.0208 (9)	0.0006 (7)	0.0006 (8)	−0.0003 (8)
C7	0.0266 (9)	0.0186 (9)	0.0210 (10)	0.0007 (7)	−0.0032 (8)	0.0036 (8)
C8	0.0301 (10)	0.0263 (10)	0.0141 (9)	−0.0050 (8)	−0.0001 (8)	−0.0016 (8)
C9	0.0318 (10)	0.0241 (10)	0.0191 (9)	0.0032 (8)	−0.0004 (8)	−0.0057 (8)
C10	0.0255 (9)	0.0197 (9)	0.0185 (9)	0.0037 (7)	−0.0007 (8)	−0.0011 (8)

Geometric parameters (Å, °)

S1—C4	1.6774 (18)	C5—C10	1.525 (2)
O1—C1	1.315 (2)	C5—H5	1.0000
O1—H1	0.845 (10)	C6—C7	1.530 (3)
O2—C1	1.225 (2)	C6—H6A	0.9900

N1—C2	1.275 (2)	C6—H6B	0.9900
N1—N2	1.363 (2)	C7—C8	1.528 (3)
N2—C4	1.370 (2)	C7—H7A	0.9900
N2—H2	0.892 (9)	C7—H7B	0.9900
N3—C4	1.330 (2)	C8—C9	1.527 (3)
N3—C5	1.458 (2)	C8—H8A	0.9900
N3—H3	0.870 (9)	C8—H8B	0.9900
C1—C2	1.491 (2)	C9—C10	1.525 (3)
C2—C3	1.488 (3)	C9—H9A	0.9900
C3—H3A	0.9800	C9—H9B	0.9900
C3—H3B	0.9800	C10—H10A	0.9900
C3—H3C	0.9800	C10—H10B	0.9900
C5—C6	1.520 (3)		
C1—O1—H1	113.7 (18)	C5—C6—H6A	109.5
C2—N1—N2	119.52 (15)	C7—C6—H6A	109.5
N1—N2—C4	117.71 (14)	C5—C6—H6B	109.5
N1—N2—H2	121.1 (14)	C7—C6—H6B	109.5
C4—N2—H2	121.2 (14)	H6A—C6—H6B	108.1
C4—N3—C5	124.97 (14)	C8—C7—C6	111.63 (15)
C4—N3—H3	120.2 (16)	C8—C7—H7A	109.3
C5—N3—H3	114.8 (16)	C6—C7—H7A	109.3
O2—C1—O1	124.08 (15)	C8—C7—H7B	109.3
O2—C1—C2	120.71 (15)	C6—C7—H7B	109.3
O1—C1—C2	115.18 (15)	H7A—C7—H7B	108.0
N1—C2—C3	126.77 (15)	C9—C8—C7	110.38 (16)
N1—C2—C1	114.80 (15)	C9—C8—H8A	109.6
C3—C2—C1	118.38 (15)	C7—C8—H8A	109.6
C2—C3—H3A	109.5	C9—C8—H8B	109.6
C2—C3—H3B	109.5	C7—C8—H8B	109.6
H3A—C3—H3B	109.5	H8A—C8—H8B	108.1
C2—C3—H3C	109.5	C10—C9—C8	111.43 (15)
H3A—C3—H3C	109.5	C10—C9—H9A	109.3
H3B—C3—H3C	109.5	C8—C9—H9A	109.3
N3—C4—N2	115.34 (15)	C10—C9—H9B	109.3
N3—C4—S1	124.83 (14)	C8—C9—H9B	109.3
N2—C4—S1	119.82 (13)	H9A—C9—H9B	108.0
N3—C5—C6	109.71 (14)	C5—C10—C9	111.06 (14)
N3—C5—C10	111.03 (14)	C5—C10—H10A	109.4
C6—C5—C10	110.79 (15)	C9—C10—H10A	109.4
N3—C5—H5	108.4	C5—C10—H10B	109.4
C6—C5—H5	108.4	C9—C10—H10B	109.4
C10—C5—H5	108.4	H10A—C10—H10B	108.0
C5—C6—C7	110.56 (15)		
C2—N1—N2—C4	175.80 (15)	C4—N3—C5—C6	−151.10 (16)
N2—N1—C2—C3	−0.7 (3)	C4—N3—C5—C10	86.1 (2)
N2—N1—C2—C1	−178.00 (14)	N3—C5—C6—C7	−179.54 (14)

O2—C1—C2—N1	169.21 (15)	C10—C5—C6—C7	−56.59 (19)
O1—C1—C2—N1	−8.9 (2)	C5—C6—C7—C8	56.5 (2)
O2—C1—C2—C3	−8.4 (2)	C6—C7—C8—C9	−55.6 (2)
O1—C1—C2—C3	173.52 (15)	C7—C8—C9—C10	55.2 (2)
C5—N3—C4—N2	−177.12 (15)	N3—C5—C10—C9	178.84 (14)
C5—N3—C4—S1	4.2 (2)	C6—C5—C10—C9	56.7 (2)
N1—N2—C4—N3	0.7 (2)	C8—C9—C10—C5	−56.1 (2)
N1—N2—C4—S1	179.49 (12)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N3—H3···N1	0.87 (1)	2.20 (2)	2.574 (2)	106 (2)
O1—H1···O2^i	0.85 (1)	1.80 (1)	2.6416 (17)	172 (3)
N2—H2···S1^{ii}	0.89 (1)	2.65 (1)	3.5384 (15)	176 (2)

Symmetry codes: (i) −*x*+1, −*y*+1, −*z*+1; (ii) −*x*+2, −*y*+3, −*z*+1.