

Acta Crystallographica Section E

Structure Reports

Online

ISSN 1600-5368

3,3'-(1-Oxopropane-1,3-diy)bis(1,3-thiazolidine-2-thione) chlorobenzene hemisolvate

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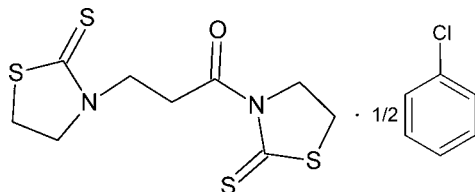
Received 24 November 2012; accepted 31 January 2013

 Key indicators: single-crystal X-ray study; $T = 123$ K; mean $\sigma(\text{C}-\text{C}) = 0.004$ Å; some non-H atoms missing; R factor = 0.044; wR factor = 0.116; data-to-parameter ratio = 20.5.

The title compound, $\text{C}_9\text{H}_{12}\text{N}_2\text{OS}_4 \cdot 0.5\text{C}_6\text{H}_5\text{Cl}$, which contains two 1,3-thiazolidine-2-thione rings, is a by-product of the synthesis of 3-acryloyl-1,3-thiazolidine-2-thione. The dihedral angle between these rings is $79.95(9)^\circ$, with both rings displaying a twisted conformation. The twist angle of the amide group is $5.6(1)^\circ$. In the crystal, the molecules are linked into [001] chains by $\text{C}-\text{H}\cdots\text{O}$ interactions. The chlorobenzene solvent molecule was found to show unresolvable disorder about a centre of inversion and its contribution to the scattering was removed with the SQUEEZE option in PLATON [Spek (2009)]. *Acta Cryst.* **D65**, 148–155].

Related literature

For N -substituted 1,3-thiazolidine-2-thione and for further synthetic details, see: Evans & Thomson (2005). For the definition of amide twist angles, see: Yamada *et al.* (1993). For details of the use of SQUEEZE, see: van der Sluis & Spek (1990).



‡ NREIP intern at NRL.

Experimental

Crystal data

 $\text{C}_9\text{H}_{12}\text{N}_2\text{OS}_4 \cdot 0.5\text{C}_6\text{H}_5\text{Cl}$
 $M_r = 348.72$

 Monoclinic, $P2_1/n$
 $a = 8.59506(18)$ Å
 $b = 9.4435(2)$ Å
 $c = 18.2640(4)$ Å
 $\beta = 92.614(2)^\circ$
 $V = 1480.90(6)$ Å³
 $Z = 4$

 Cu $K\alpha$ radiation
 $\mu = 6.68$ mm⁻¹
 $T = 123$ K
 $0.45 \times 0.25 \times 0.14$ mm

Data collection

Agilent Xcalibur (Ruby, Gemini) diffractometer

 Absorption correction: multi-scan [*CrysAlis PRO* (Agilent, 2012), based on expressions derived by

 Clark & Reid (1995)]
 $T_{\min} = 0.757$, $T_{\max} = 1.000$
 5329 measured reflections
 2971 independent reflections
 2486 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.029$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.044$
 $wR(F^2) = 0.116$
 $S = 1.05$

2971 reflections

145 parameters

H-atom parameters constrained

 $\Delta\rho_{\max} = 0.44$ e Å⁻³
 $\Delta\rho_{\min} = -0.32$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{C9}-\text{H9A}\cdots\text{O1}^i$	0.99	2.55	3.340 (4)	137

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

Data collection: *CrysAlis PRO* (Agilent, 2012); 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: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

We thank The Office Of Naval Research for financial support. RJB wishes to acknowledge the NSF-MRI program (grant CHE-0619278) for funds to purchase the diffractometer.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB7002).

References

- Agilent (2012). *CrysAlis PRO*. Agilent Technologies, Yarnton, England.
 Clark, R. C. & Reid, J. S. (1995). *Acta Cryst.* **A51**, 887–897.
 Evans, D. & Thomson, R. (2005). *J. Am. Chem. Soc.* **127**, 10506–10507.
 Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
 Sluis, P. van der & Spek, A. L. (1990). *Acta Cryst.* **A46**, 194–201.
 Spek, A. L. (2009). *Acta Cryst.* **D65**, 148–155.
 Yamada, S. (1993). *Angew. Chem. Int. Ed. Engl.* **32**, 1083–1085.

supporting information

Acta Cryst. (2013). E69, o375 [doi:10.1107/S1600536813003292]

3,3'-(1-Oxopropane-1,3-diyl)bis(1,3-thiazolidine-2-thione) chlorobenzene hemisolvate

Christine Franzel, Andrew Purdy and Ray J. Butcher

S1. Comment

The title compound, 3,3'-(1-oxopropane-1,3-diyl)bis(1,3-thiazolidine-2-thione), is a by-product of the synthesis of 3-acryloyl-1,3-thiazolidine-2-thione. The formation of the title compound results from a nucleophilic attack of the nitrogen of excess 1,3-thiazolidine-2-thione, on the terminal alkene of 3-acryloyl-1,3-thiazolidine-2-thione.

The crystallographic data show both of the thiazolidine-2-thione rings display a twist conformation; C2 and C3 are displaced 0.269 (4) Å and -0.070 (4) Å respectively from the mean N1 C1 S1 S2 plane, while C8 and C9 are displaced 0.118 (4) Å and -0.175 (4) Å respectively from the mean N2 C7 S3 S4 plane. These two planes form a dihedral angle of 79.97 (9)°. The amide present in the title compound is nearly flat, with a twist angle about the C4–N1 bond of 5.6 (1)° (calculated according to the definition given by Yamada 1993).

Figure 2 shows the molecular packing for C₉H₁₂N₂OS₄, modified using the SQUEEZE function. The void in the center of the unit cell contains a disordered molecule of chlorobenzene, the recrystallization solvent used in this experiment, lying on a center of inversion.

S2. Experimental

The procedure for the synthesis of 3-acryloyl-1,3-thiazolidine-2-thione was modeled after that of Evans & Thomson (2005). Briefly, 1,3-thiazolidine-2-thione (2.27 g, 19.0 mmol) and Et₃N (1.93 g, 18.9 mmol) in CH₂Cl₂ (50 ml) were added to a round-bottom flask with an egg-shaped stir bar and a pinch of phenothiazine inhibitor. The flask was placed in an EtOH/dry ice bath (-78°C) and kept under N₂. Acryloyl chloride (1.71 g, 18.9 mmol) in CH₂Cl₂ (10 mL) was added dropwise to the flask over 5 minutes. The reaction mixture was slowly warmed to room temperature and stirred for 1 h. The yellow product mixture was then washed with H₂O, and the aqueous layer was extracted twice with CH₂Cl₂. The combined organic layers were extracted twice with saturated NaHCO₃, once more with H₂O, dried (MgSO₄), filtered, and concentrated. One grain of CuCl₂ was added to the flask as polymerization inhibitor. The reaction mixture was poured into CHCl₃, and the title compound precipitated as a light-yellow solid. The solid title compound was recrystallized from chlorobenzene solution to give almost colorless prisms.

NMR Spectrum of title compound (CH₂Cl₂ solution): ¹H 4.539, 4.162, 4.044, 3.697, 3.302, 3.275 (t, 2H); ¹³C 202.26 (C=S), 196.85 (C=S), 172.06 (C=O), 57.73, 56.09, 44.90, 35.63, 28.43, 27.65 (CH₂). IR Spectrum (film on KBr): 2988(vw), 2930(w), 2929(vw), 2890(vw), 2854(vw) (C—H), 1690 (s, C=O), 1488 (s), 1453 (w), 1424 (w), 1365 (m), 1316 (s), 1278 (s), 1224 (s), 1157(s), 1050 (m), 1027 (w), 995 (w), 884 (w).

S3. Refinement

H atoms were placed in calculated positions with C—H = 0.99 Å for the CH₂ H atoms, and refined using riding model, with *U*_{iso}(H) = 1.2U_{eq}(C,N). There was a molecule of chlorobenzene located on an inversion center but disordered over

multiple conformations. After unsuccessful attempts to model this SQUEEZE was used to remove its contribution (Van der Sluis & Spek, 1990).

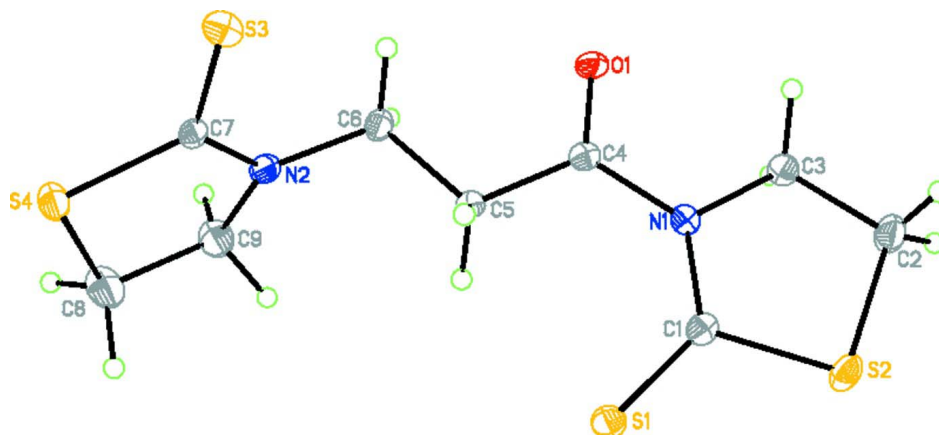


Figure 1

Diagram of the title compound showing 50% displacement ellipsoids.

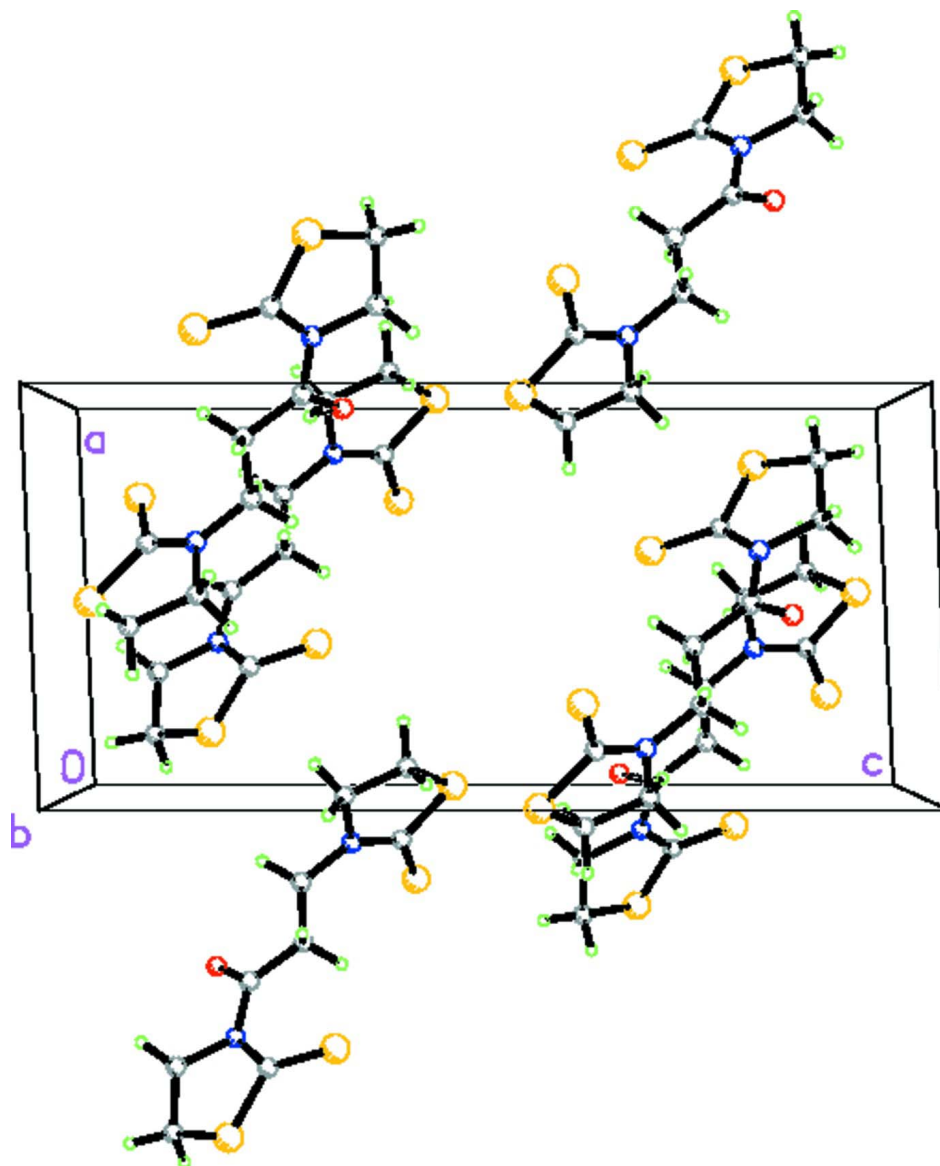


Figure 2

Molecular packing of $C_9H_{12}N_2OS_4$, viewed down the b axis.

3,3'-(1-Oxopropane-1,3-diy)bis(1,3-thiazolidine-2-thione) chlorobenzene hemisolvate

Crystal data

$C_9H_{12}N_2OS_4 \cdot 0.5C_6H_5Cl$

$M_r = 348.72$

Monoclinic, $P2_1/n$

$a = 8.59506$ (18) Å

$b = 9.4435$ (2) Å

$c = 18.2640$ (4) Å

$\beta = 92.614$ (2)°

$V = 1480.90$ (6) Å³

$Z = 4$

$F(000) = 724$

$D_x = 1.564$ Mg m⁻³

Cu $K\alpha$ radiation, $\lambda = 1.54184$ Å

Cell parameters from 2930 reflections

$\theta = 4.7\text{--}75.6^\circ$

$\mu = 6.68$ mm⁻¹

$T = 123$ K

Prism, colorless

$0.45 \times 0.25 \times 0.14$ mm

Data collection

Agilent Xcalibur (Ruby, Gemini) diffractometer
 Radiation source: Enhance (Cu) X-ray Source
 Graphite monochromator
 Detector resolution: 10.5081 pixels mm⁻¹
 ω scans
 Absorption correction: multi-scan [CrysAlis PRO (Agilent, 2012), based on expressions derived by Clark & Reid (1995)]

$T_{\min} = 0.757$, $T_{\max} = 1.000$
 5329 measured reflections
 2971 independent reflections
 2486 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.029$
 $\theta_{\max} = 75.8^\circ$, $\theta_{\min} = 4.9^\circ$
 $h = -9 \rightarrow 10$
 $k = -11 \rightarrow 10$
 $l = -22 \rightarrow 20$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.044$
 $wR(F^2) = 0.116$
 $S = 1.05$
 2971 reflections
 145 parameters
 0 restraints
 Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map
 Hydrogen site location: inferred from neighbouring sites
 H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0574P)^2 + 1.0183P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.44 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.32 \text{ e } \text{\AA}^{-3}$

Special details

Experimental. CrysAlisPro, Agilent Technologies, Version 1.171.35.21 (release 20-01-2012 CrysAlis171 .NET) (compiled Jan 23 2012, 18:06:46) Analytical numeric absorption correction using a multifaceted crystal model based on expressions derived by R.C. Clark & J.S. Reid. (Clark, R. C. & Reid, J. S. (1995). Acta Cryst. A51, 887-897)

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 (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
S1	0.38391 (7)	0.58687 (8)	0.30163 (4)	0.02748 (18)
S2	0.16697 (8)	0.60275 (8)	0.17409 (4)	0.02960 (19)
S3	0.75412 (7)	0.06152 (7)	0.39778 (4)	0.02613 (18)
S4	1.01178 (8)	0.25235 (8)	0.44956 (4)	0.02741 (18)
O1	0.5444 (2)	0.2367 (2)	0.15272 (10)	0.0247 (4)
N1	0.3858 (2)	0.4161 (2)	0.17961 (11)	0.0194 (4)
N2	0.8680 (3)	0.2837 (2)	0.32473 (12)	0.0232 (5)
C1	0.3274 (3)	0.5256 (3)	0.22011 (14)	0.0210 (5)
C2	0.1553 (4)	0.4708 (4)	0.10302 (18)	0.0398 (8)
H2A	0.0692	0.4039	0.1114	0.048*
H2B	0.1363	0.5160	0.0545	0.048*
C3	0.3092 (3)	0.3939 (3)	0.10594 (14)	0.0235 (5)
H3A	0.2922	0.2915	0.0971	0.028*

H3B	0.3762	0.4309	0.0676	0.028*
C4	0.5170 (3)	0.3302 (3)	0.19528 (14)	0.0193 (5)
C5	0.6201 (3)	0.3555 (3)	0.26305 (13)	0.0180 (5)
H5A	0.5621	0.3338	0.3073	0.022*
H5B	0.6522	0.4561	0.2653	0.022*
C6	0.7637 (3)	0.2609 (3)	0.26076 (14)	0.0254 (5)
H6A	0.7308	0.1604	0.2590	0.030*
H6B	0.8196	0.2815	0.2158	0.030*
C7	0.8692 (3)	0.2009 (3)	0.38392 (13)	0.0195 (5)
C8	1.0683 (4)	0.4060 (4)	0.39771 (18)	0.0404 (8)
H8A	1.0306	0.4937	0.4206	0.048*
H8B	1.1831	0.4111	0.3959	0.048*
C9	0.9945 (4)	0.3887 (3)	0.32101 (18)	0.0355 (7)
H9A	0.9523	0.4804	0.3030	0.043*
H9B	1.0732	0.3558	0.2869	0.043*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0230 (3)	0.0325 (4)	0.0272 (3)	0.0043 (3)	0.0034 (2)	-0.0095 (3)
S2	0.0241 (3)	0.0368 (4)	0.0281 (3)	0.0123 (3)	0.0033 (2)	-0.0017 (3)
S3	0.0224 (3)	0.0275 (3)	0.0290 (3)	-0.0045 (2)	0.0071 (2)	-0.0041 (3)
S4	0.0287 (3)	0.0288 (4)	0.0242 (3)	-0.0057 (3)	-0.0048 (2)	0.0034 (3)
O1	0.0292 (9)	0.0204 (9)	0.0244 (9)	0.0041 (8)	0.0012 (7)	-0.0059 (7)
N1	0.0190 (9)	0.0212 (10)	0.0180 (9)	-0.0019 (8)	0.0027 (7)	0.0001 (8)
N2	0.0277 (11)	0.0201 (11)	0.0216 (10)	0.0042 (9)	-0.0003 (8)	-0.0007 (8)
C1	0.0167 (11)	0.0217 (12)	0.0252 (12)	-0.0014 (9)	0.0066 (9)	0.0029 (10)
C2	0.0347 (16)	0.0485 (19)	0.0350 (16)	0.0171 (15)	-0.0120 (13)	-0.0150 (14)
C3	0.0253 (12)	0.0265 (13)	0.0189 (12)	0.0016 (11)	0.0019 (9)	-0.0003 (10)
C4	0.0189 (11)	0.0175 (11)	0.0218 (12)	-0.0024 (9)	0.0053 (9)	0.0025 (9)
C5	0.0201 (11)	0.0170 (11)	0.0170 (11)	0.0000 (9)	0.0024 (9)	0.0004 (9)
C6	0.0257 (12)	0.0271 (14)	0.0228 (12)	0.0075 (11)	-0.0038 (10)	-0.0027 (11)
C7	0.0157 (10)	0.0224 (12)	0.0205 (11)	0.0063 (9)	0.0019 (9)	-0.0045 (9)
C8	0.0521 (19)	0.0308 (16)	0.0373 (17)	-0.0188 (14)	-0.0080 (14)	0.0101 (13)
C9	0.0443 (17)	0.0287 (15)	0.0327 (15)	-0.0086 (13)	-0.0064 (13)	0.0085 (12)

Geometric parameters (Å, °)

S1—C1	1.650 (3)	C2—H2B	0.9900
S2—C1	1.741 (3)	C3—H3A	0.9900
S2—C2	1.799 (3)	C3—H3B	0.9900
S3—C7	1.673 (3)	C4—C5	1.508 (3)
S4—C7	1.744 (3)	C5—C6	1.526 (3)
S4—C8	1.811 (3)	C5—H5A	0.9900
O1—C4	1.206 (3)	C5—H5B	0.9900
N1—C1	1.379 (3)	C6—H6A	0.9900
N1—C4	1.408 (3)	C6—H6B	0.9900
N1—C3	1.486 (3)	C8—C9	1.520 (4)

N2—C7	1.334 (4)	C8—H8A	0.9900
N2—C6	1.456 (3)	C8—H8B	0.9900
N2—C9	1.475 (4)	C9—H9A	0.9900
C2—C3	1.508 (4)	C9—H9B	0.9900
C2—H2A	0.9900		
C1—S2—C2	94.31 (13)	C4—C5—H5A	109.8
C7—S4—C8	93.47 (14)	C6—C5—H5A	109.8
C1—N1—C4	129.1 (2)	C4—C5—H5B	109.8
C1—N1—C3	115.8 (2)	C6—C5—H5B	109.8
C4—N1—C3	114.9 (2)	H5A—C5—H5B	108.3
C7—N2—C6	123.1 (2)	N2—C6—C5	111.2 (2)
C7—N2—C9	116.9 (2)	N2—C6—H6A	109.4
C6—N2—C9	119.4 (2)	C5—C6—H6A	109.4
N1—C1—S1	130.4 (2)	N2—C6—H6B	109.4
N1—C1—S2	110.76 (19)	C5—C6—H6B	109.4
S1—C1—S2	118.87 (15)	H6A—C6—H6B	108.0
C3—C2—S2	106.8 (2)	N2—C7—S3	127.0 (2)
C3—C2—H2A	110.4	N2—C7—S4	111.9 (2)
S2—C2—H2A	110.4	S3—C7—S4	121.13 (15)
C3—C2—H2B	110.4	C9—C8—S4	106.6 (2)
S2—C2—H2B	110.4	C9—C8—H8A	110.4
H2A—C2—H2B	108.6	S4—C8—H8A	110.4
N1—C3—C2	108.4 (2)	C9—C8—H8B	110.4
N1—C3—H3A	110.0	S4—C8—H8B	110.4
C2—C3—H3A	110.0	H8A—C8—H8B	108.6
N1—C3—H3B	110.0	N2—C9—C8	107.9 (2)
C2—C3—H3B	110.0	N2—C9—H9A	110.1
H3A—C3—H3B	108.4	C8—C9—H9A	110.1
O1—C4—N1	117.9 (2)	N2—C9—H9B	110.1
O1—C4—C5	121.4 (2)	C8—C9—H9B	110.1
N1—C4—C5	120.7 (2)	H9A—C9—H9B	108.4
C4—C5—C6	109.3 (2)		
C4—N1—C1—S1	-3.8 (4)	N1—C4—C5—C6	-172.5 (2)
C3—N1—C1—S1	-177.4 (2)	C7—N2—C6—C5	97.3 (3)
C4—N1—C1—S2	177.3 (2)	C9—N2—C6—C5	-92.1 (3)
C3—N1—C1—S2	3.7 (3)	C4—C5—C6—N2	179.0 (2)
C2—S2—C1—N1	8.0 (2)	C6—N2—C7—S3	-1.3 (4)
C2—S2—C1—S1	-170.96 (19)	C9—N2—C7—S3	-172.1 (2)
C1—S2—C2—C3	-16.8 (3)	C6—N2—C7—S4	177.92 (19)
C1—N1—C3—C2	-16.4 (3)	C9—N2—C7—S4	7.1 (3)
C4—N1—C3—C2	169.0 (2)	C8—S4—C7—N2	4.2 (2)
S2—C2—C3—N1	20.6 (3)	C8—S4—C7—S3	-176.58 (19)
C1—N1—C4—O1	177.7 (2)	C7—S4—C8—C9	-13.2 (3)
C3—N1—C4—O1	-8.6 (3)	C7—N2—C9—C8	-17.1 (4)
C1—N1—C4—C5	-2.6 (4)	C6—N2—C9—C8	171.7 (3)
C3—N1—C4—C5	171.0 (2)	S4—C8—C9—N2	18.3 (3)

O1—C4—C5—C6 7.2 (3)

Hydrogen-bond geometry (Å, °)

<i>D—H...A</i>	<i>D—H</i>	<i>H...A</i>	<i>D...A</i>	<i>D—H...A</i>
C9—H9A...O1 ⁱ	0.99	2.55	3.340 (4)	137

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