

Received 28 April 2017

Accepted 23 May 2017

Edited by W. T. A. Harrison, University of
Aberdeen, Scotland**Keywords:** crystal structure; thiazolidine; thio-
phene; rhodanine; polythiophene.**CCDC reference:** 1551679**Supporting information:** this article has
supporting information at journals.iucr.org/e

Crystal structure of *N*-(4-oxo-2-sulfanylidene-1,3-thiazolidin-3-yl)-2-(thiophen-3-yl)acetamide

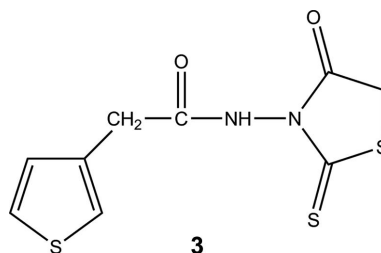
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The title compound, C₉H₈N₂O₂S₃, crystallizes with two molecules (*A* and *B*) in the asymmetric unit. Both have similar conformations (overlay r.m.s. deviation = 0.209 Å) and are linked by an N—H···O hydrogen bond. In both molecules, the thiophene rings show orientational disorder, with occupancy factors of 0.6727 (17) and 0.3273 (17) for molecule *A*, and 0.7916 (19) and 0.2084 (19) for molecule *B*. The five-membered rings make an angle of 79.7 (2)° in molecule *A* and an angle of 66.8 (2)° in molecule *B*. In the crystal, chains of molecules running along the *a*-axis direction are linked by N—H···O hydrogen bonds. The interaction of adjacent chains through N—H···O hydrogen bonds leads to two types of ring structures containing four molecules and described by the graph-set motifs R₄⁴(18) and R₄²(14).

1. Chemical context

Thiophene, C₄H₄S, belongs to a class of aromatic five-membered heterocycles containing one S heteroatom. Thiophene and its derivatives occur in petroleum or coal (Orr & White, 1990). Thiophene-based compounds have applications in modern drug design (Santagati *et al.*, 1994), electronic and optoelectronic devices (Barbarella *et al.*, 2005), and conductive and electroluminescent polymers (Friend *et al.*, 1999). Also, several reviews of various aspects of thiophene coordination and reactivity in transition-metal complexes have been reported (Barbarella *et al.*, 2005).



Derivatives of rhodanine (or 2-thioxo-1,3-thiazolidin-4-one) have interesting pharmacological properties, such as the drug Epalrestat, which is an aldose reductase inhibitor used to treat diabetic neuropathy (Tomašić & Mašič, 2012). Some other rhodanine derivatives were designed and synthesized for detecting tau pathology in the brains of patients with Alzheimer's disease (Ono *et al.*, 2011).

As a continuation of our research (Nguyen *et al.*, 2016; Vu *et al.*, 2016) on the chemical, physical and biological properties of new polythiophenes, a new thiophene monomer containing

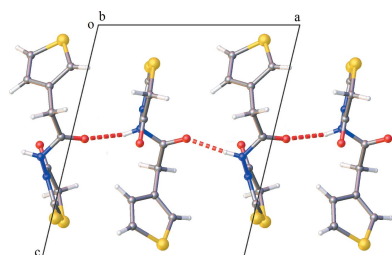


Table 1

Hydrogen-bond geometry (Å, °).

*Cg*₁ and *Cg*₂ are the centroids of the S1A/C1A–C4A and S11A/C11A–C14A rings, respectively.

<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>
N1–H1···O11	0.824 (19)	1.973 (19)	2.7923 (16)	173.1 (18)
N11–H11···O1 ⁱ	0.819 (19)	2.189 (19)	2.8436 (16)	137.1 (16)
N11–H11···O2 ⁱⁱ	0.819 (19)	2.519 (18)	3.0965 (16)	128.6 (15)
C5–H5A···O12 ⁱⁱⁱ	0.99	2.46	3.3901 (19)	156
C9–H9A···O2 ^{iv}	0.99	2.53	3.2443 (19)	129
C9–H9B···S13 ⁱⁱ	0.99	2.81	3.6570 (17)	144
C15–H15A···O2 ⁱⁱ	0.99	2.37	3.2862 (19)	154
C9–H9A··· <i>Cg</i> ₁ ^{iv}	0.99	2.73	3.276 (3)	115
C19–H19A··· <i>Cg</i> ₂ ⁱⁱⁱ	0.99	2.77	3.480 (2)	129

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

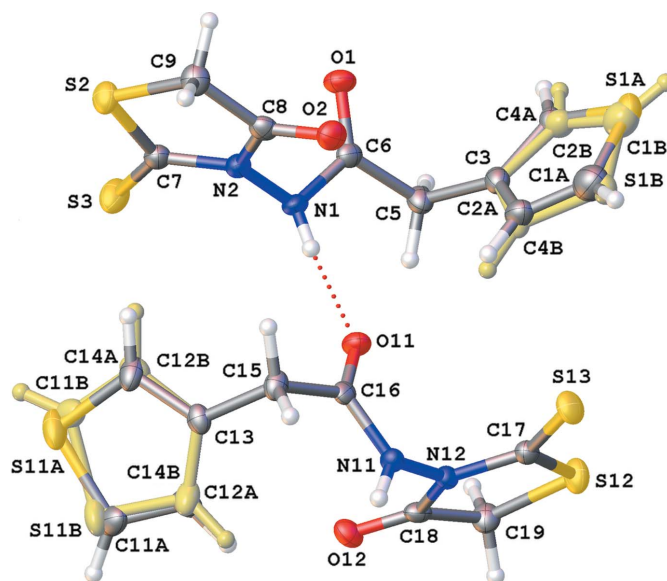
rhodanine has been prepared. In the presence of FeCl₃, thiophene monomers can be polymerized by C–C bond formation between the 2- and 5-positions of two subsequent thiophene monomers, resulting in an extended π -conjugated system. We present here the synthesis and crystal structure of *N*-(4-oxo-2-sulfanylidene-1,3-thiazolidin-3-yl)-2-(thiophen-3-yl)acetamide, **3**.

2. Structural commentary

Crystals of the title compound belong to the triclinic space group $P\bar{1}$ with two independent molecules (*A* and *B*) per asymmetric unit (Fig. 1). In both molecules, the thiophene ring is disordered over two positions by a rotation of approximately 180° around the C5–C3 or C15–C13 bond for molecules *A* and *B*, respectively [occupancy factors = 0.6727 (17) and 0.3273 (17) for molecule *A*, and 0.7916 (19) and 0.2084 (19) for molecule *B*]. In the current discussion, only the major components will be considered. The 1,3-thiazolidine ring is almost planar (r.m.s. deviation = 0.020 Å for ring S2/N2/C7–C9 and 0.010 Å for ring S12/N12/C17–C19) with the N3-substituents N1 [0.141 (1) Å] and N11 [0.100 (1) Å] situated in the same plane (deviations from plane given in parenthesis). Both thiophene rings are also planar as expected (r.m.s. deviation = 0.011 Å for ring S1A/C1A–C4A and 0.002 Å for ring S11A/C11A–C14A), with the substituents C5 [–0.065 (2) Å] and C15 [0.001 (1) Å] coplanar. In molecule *A*, the heterocyclic rings make an angle of 79.7 (2)°; in molecule *B*, this angle is 66.8 (2)°. Also, the amide group and the 1,3-thiazolidine ring are oriented almost perpendicular to each other. In molecule *A*, the plane through the atoms of the amide group (N1/C6/O1) makes an angle of 76.32 (8)° with the best plane through the 1,3-thiazolidine ring; for molecule *B*, this angle is 83.88 (6)°. Both molecules in the asymmetric unit are linked by an N1–H1···O11 hydrogen bond (Table 1 and Fig. 1).

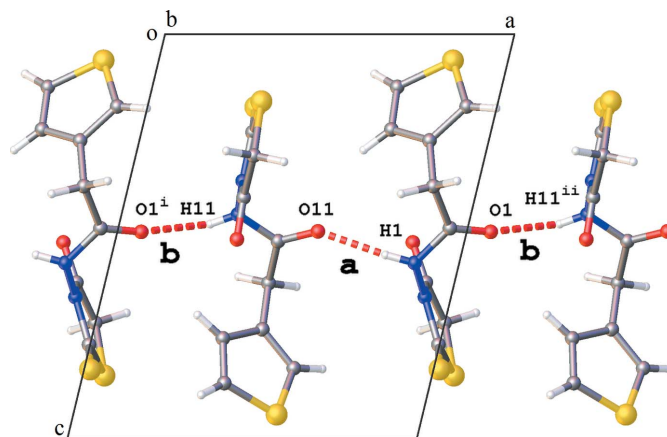
3. Supramolecular features

The crystal packing is governed by hydrogen bonding. Chains of molecules are formed along the *a*-axis direction by alter-


Figure 1

View of the asymmetric unit of the title compound, showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms are shown as small circles of arbitrary radii. The minor component of the disordered thiophene rings is shown in pale yellow.

nating N1–H1···O11 and N11–H11···O1 hydrogen bonds (Table 1 and Fig. 2). The interaction of adjacent chains through N11–H11···O2 hydrogen bonds results in two different types of ring structures, each containing four molecules: (i) a ring structure of graph-set motif $R_4^4(18)$ showing also additional C–H···O and C–H···S interactions (Table 1 and Fig. 3), and (ii) a ring structure with graph-set motif $R_4^2(14)$ (Fig. 4). The packing shows a number of additional C–H···O, C–H···S and weak C–H··· π interactions (Table 1). The crystal packing contains no voids.


Figure 2

Part of the crystal packing of the title compound, showing a chain of molecules along the *a* axis formed by N–H···O hydrogen-bond interactions **a** and **b** [see Table 1; symmetry codes: (i) $x - 1, y, z$; (ii) $x + 1, y, z$].

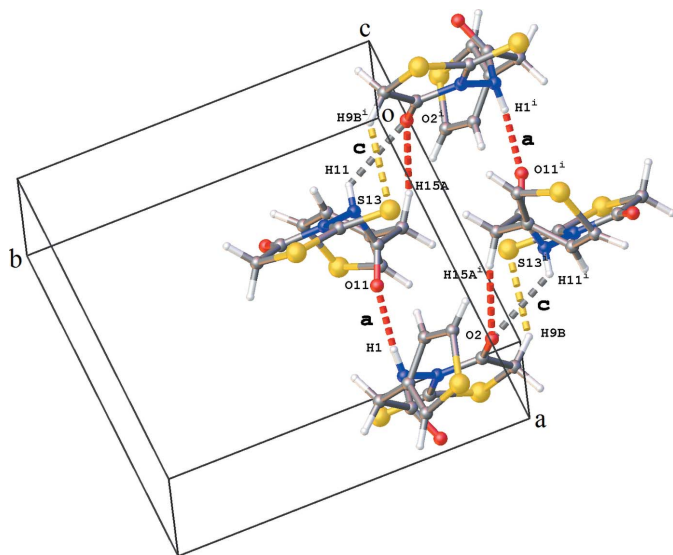


Figure 3
Ring of graph-set motif $R_4^d(18)$ formed by N–H...O hydrogen-bond interactions **a** and **c** [see Table 1; symmetry code: (i) $-x + 1, -y, -z + 1$].

4. Database survey

A search of the Cambridge Structural Database (CSD, Version 5.38, last update February 2017; Groom *et al.*, 2016) for structures containing an *N*-substituted 2-thioxo-1,3-thiazolidin-4-one ring gave 26 hits (169 hits when substituents at the 5-position are also allowed). In all cases, the 1,3-thiazolidine ring can be considered to be planar, as the largest deviation from the best plane through the ring atoms was only 0.070 Å [for the complex bis(rhodanine)copper(I) iodide; refcode VICJUM; Moers *et al.*, 1986]. The substituent at the N3 position is situated in the 1,3-thiazolidine plane, with a largest deviation of 0.174 Å for the case with $-\text{NH}_2$ as substituent (refcode EDEPUZ01; Jabeen *et al.*, 2007).

Rotational disorder in 3- CH_2 -thiophene fragments is frequently observed (25 structures of the 67 fragments present in the CSD).

5. Synthesis and crystallization

The reaction scheme to synthesize the title compound, **3**, is given in Fig. 5.

5.1. Synthesis of methyl 2-(thiophen-3-yl)acetate, **1**

Methyl thiophene-2-acetate, **1** (5 mmol), was added to an excess of hydrazine hydrate (40 mmol) in ethanol (20 ml). The mixture was refluxed for 6 h. The reaction mixture was

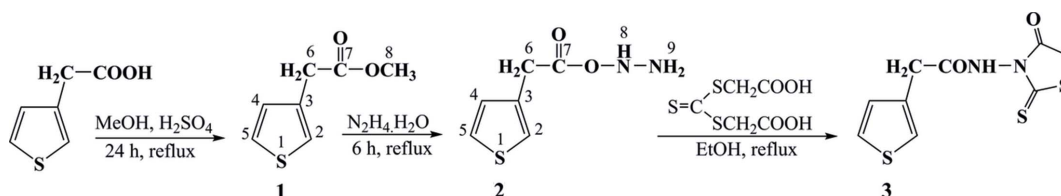


Figure 5
Reaction scheme for the title compound.

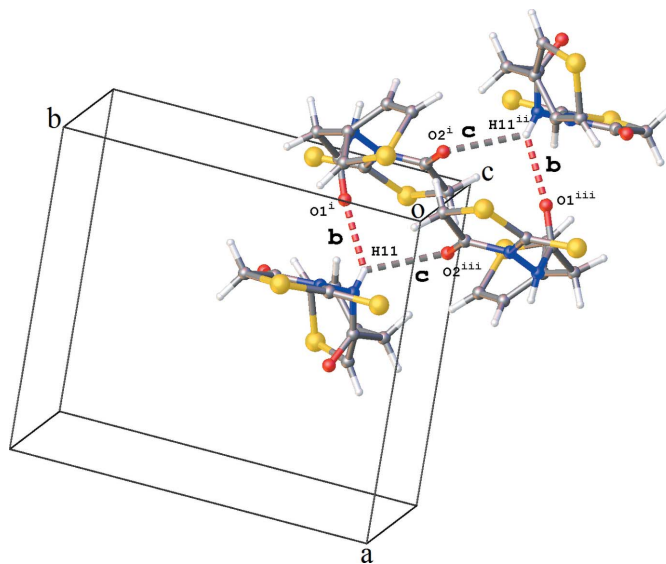


Figure 4
Ring of graph-set motif $R_4^d(14)$ formed by N–H...O hydrogen-bond interactions **b** and **c** [see Table 1; symmetry codes: (i) $x - 1, y, z$; (ii) $-x, -y, -z + 1$; (iii) $-x + 1, -y, -z + 1$].

allowed to cool. The resulting precipitate was filtered and recrystallized from ethanol solution to give 0.57 g (yield 74%) of hydrazide **2** in the form of white crystals (m.p. 343 K). IR (Nicolet Impact 410 FTIR, KBr, cm^{-1}): 3323, 3068 (ν_{NH}), 3068, 2957 (ν_{CH}), 1641 ($\nu_{\text{C=O}}$), 1526 ($\nu_{\text{C=C}}$ thiophene). ^1H NMR [Bruker XL-500, 500 MHz, d_6 -DMSO, δ (ppm), J (Hz)]: 7.22 (*dd*, 1H, $^4J = 1.0$, $^5J = 2.0$, H²), 7.01 (*d*, 1H, $^5J = 5.0$, H⁴), 7.43 (*dd*, 1H, $^2J = 3.0$, $^4J = 4.5$, H⁵), 3.32 (*s*, 2H, H⁶), 9.14 (*s*, 1H, H⁸), 4.19 (*s*, 2H, H⁹). ^{13}C NMR [Bruker XL-500, 125 MHz, d_6 -DMSO, δ (ppm)]: 122.06 (C²), 135.95 (C³), 128.62 (C⁴), 125.59 (C⁵), 35.10 (C⁷), 169.17 (C⁸). Calculation for $\text{C}_6\text{H}_8\text{O}_2\text{N}_2\text{S}$: $M = 172$ au.

5.2. Synthesis of 2-(thiophen-3-yl)acetohydrazide, **2**

Methyl thiophene-2-acetate, **1** (5 mmol), was added to an excess of hydrazine hydrate (40 mmol) in ethanol (20 ml). The mixture was refluxed for 6 h. The reaction mixture was allowed to cool. The resulting precipitate was filtered and recrystallized from ethanol solution to give 0.57 g (yield 74%) of hydrazide **2** in the form of white crystals (m.p. 343 K). IR (Nicolet Impact 410 FTIR, KBr, cm^{-1}): 3323, 3068 (ν_{NH}), 3068, 2957 (ν_{CH}), 1641 ($\nu_{\text{C=O}}$), 1526 ($\nu_{\text{C=C}}$ thiophene). ^1H NMR [Bruker XL-500, 500 MHz, d_6 -DMSO, δ (ppm), J (Hz)]: 7.22 (*dd*, 1H, $^4J = 1.0$, $^5J = 2.0$, H²), 7.01 (*d*, 1H, $^5J = 5.0$, H⁴), 7.43 (*dd*, 1H, $^2J = 3.0$, $^4J = 4.5$, H⁵), 3.32 (*s*, 2H, H⁶), 9.14 (*s*, 1H,

H⁸), 4.19 (s, 2H, H⁹). ¹³C NMR [Bruker XL-500, 125 MHz, *d*₆-DMSO, δ (ppm)]: 122.06 (C²), 135.95 (C³), 128.62 (C⁴), 125.59 (C⁵), 35.10 (C⁷), 169.17 (C⁸). Calculation for C₆H₈O₂N₂S: *M* = 172 au.

5.3. Synthesis of *N*-(4-oxo-2-sulfanylidene-1,3-thiazolidin-3-yl)-2-(thiophen-3-yl)acetamide, **3**

A mixture of hydrazide **2** (10 mmol) and thiocarbonylbis-thioglycolic acid (10 mmol) in ethanol (5 ml) was refluxed for 8 h. After cooling, the resulting precipitate was filtered off, dried and recrystallized from ethanol solution to give 1.66 g (yield 61%) of **3** as a pale-yellow crystals (m.p. 372 K). IR (Nicolet Impact 410 FTIR, KBr, cm⁻¹): 3442, 3292, 3226 (ν_{NH}), 3148, 2965, 2921 (ν_{CH}), 1727, 1684 ($\nu_{\text{C=O}}$), 1614, 1532 ($\nu_{\text{C=C}}$ thiophene), 1244, 1177 ($\nu_{\text{C=S}}$). Calculation for C₉H₈O₂N₂S₃: *M* = 272 au.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. Both thiophene rings are disordered over two positions by a rotation of approximately 180° around the C5—C3 or C15—C13 bond for molecules *A* and *B*, respectively. The final occupancy factors are 0.6727 (17) and 0.3273 (17) for molecule *A*, and 0.7916 (19) and 0.2084 (19) for molecule *B*. Bond lengths and angles in the disordered thiophene rings were restrained to target values derived from mean values observed in 3-CH₂-thiophene fragments in the CSD (Groom *et al.*, 2016). The same anisotropic displacement parameters were used for equivalent atoms in the disordered thiophene rings (*e.g.* EADP C1A C1B). The H atoms attached to atoms N1 and N11 were found in the difference density Fourier map and refined freely. The other H atoms were placed in idealized positions and refined in riding mode, with *U*_{iso}(H) values assigned as 1.2*U*_{eq} of the parent atoms, with C—H distances of 0.95 (aromatic) and 0.99 Å (CH₂). In the final cycles of refinement, four outliers were omitted.

Acknowledgements

LVM thanks VLIR–UOS (project ZEIN2014Z182) for financial support.

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Table 2
Experimental details.

Crystal data	
Chemical formula	C ₉ H ₈ N ₂ O ₂ S ₃
<i>M</i> _r	272.35
Crystal system, space group	Triclinic, <i>P</i> $\bar{1}$
Temperature (K)	100
<i>a</i> , <i>b</i> , <i>c</i> (Å)	9.6205 (3), 10.8252 (3), 11.5073 (3)
α , β , γ (°)	97.836 (2), 102.720 (2), 95.047 (2)
<i>V</i> (Å ³)	1149.42 (6)
<i>Z</i>	4
Radiation type	Mo <i>K</i> α
μ (mm ⁻¹)	0.63
Crystal size (mm)	0.22 × 0.07 × 0.04
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan (<i>SADABS</i> ; Bruker, 2014)
<i>T</i> _{min} , <i>T</i> _{max}	0.691, 0.746
No. of measured, independent and observed [<i>I</i> > 2 σ (<i>I</i>)] reflections	37647, 6098, 4985
<i>R</i> _{int}	0.042
(<i>sin</i> θ / λ) _{max} (Å ⁻¹)	0.682
Refinement	
<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.032, 0.077, 1.03
No. of reflections	6098
No. of parameters	323
No. of restraints	40
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ (e Å ⁻³)	0.38, -0.25

Computer programs: *APEX2* (Bruker, 2014), *SAINT* (Bruker, 2013), *SHELXS1997* (Sheldrick, 2008), *SHELXL* (Sheldrick, 2015) and *OLEX2* (Dolomanov *et al.*, 2009).

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supporting information

Acta Cryst. (2017). E73, 901-904 [https://doi.org/10.1107/S2056989017007629]

Crystal structure of *N*-(4-oxo-2-sulfanylidene-1,3-thiazolidin-3-yl)-2-(thiophen-3-yl)acetamide

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Computing details

Data collection: *APEX2* (Bruker, 2014); cell refinement: *S SAINT* v8.34A (Bruker, 2013); data reduction: *S SAINT* v8.34A (Bruker, 2013); program(s) used to solve structure: *SHELXS1997* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL* (Sheldrick, 2015); molecular graphics: *Olex2* (Dolomanov *et al.*, 2009); software used to prepare material for publication: *Olex2* (Dolomanov *et al.*, 2009).

N-(4-Oxo-2-sulfanylidene-1,3-thiazolidin-3-yl)-2-(thiophen-3-yl)acetamide

Crystal data

$C_9H_8N_2O_2S_3$

$M_r = 272.35$

Triclinic, $P\bar{1}$

$a = 9.6205$ (3) Å

$b = 10.8252$ (3) Å

$c = 11.5073$ (3) Å

$\alpha = 97.836$ (2)°

$\beta = 102.720$ (2)°

$\gamma = 95.047$ (2)°

$V = 1149.42$ (6) Å³

$Z = 4$

$F(000) = 560$

$D_x = 1.574$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 9925 reflections

$\theta = 3.1\text{--}30.6^\circ$

$\mu = 0.63$ mm⁻¹

$T = 100$ K

Block, colourless

$0.22 \times 0.07 \times 0.04$ mm

Data collection

Bruker APEX-II CCD
diffractometer

φ and ω scans

Absorption correction: multi-scan
(SADABS; Bruker, 2014)

$T_{\min} = 0.691$, $T_{\max} = 0.746$

37647 measured reflections

6098 independent reflections

4985 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.042$

$\theta_{\max} = 29.0^\circ$, $\theta_{\min} = 2.9^\circ$

$h = -13 \rightarrow 13$

$k = -14 \rightarrow 14$

$l = -15 \rightarrow 15$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.032$

$wR(F^2) = 0.077$

$S = 1.03$

6098 reflections

323 parameters

40 restraints

Primary atom site location: structure-invariant
direct methods

Hydrogen site location: mixed

H atoms treated by a mixture of independent
and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0367P)^2 + 0.3868P]$

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

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

$$\Delta\rho_{\max} = 0.38 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.25 \text{ e } \text{\AA}^{-3}$$

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds 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>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
C1A	0.7012 (6)	0.0875 (6)	0.1304 (5)	0.0435 (14)	0.6727 (17)
H1A	0.627681	0.019090	0.098279	0.052*	0.6727 (17)
C1B	0.8309 (14)	0.1396 (12)	0.0779 (11)	0.0435 (14)	0.3273 (17)
H1B	0.865405	0.109102	0.009449	0.052*	0.3273 (17)
C2A	0.7136 (6)	0.1688 (5)	0.2354 (6)	0.0292 (11)	0.6727 (17)
H2A	0.648572	0.161127	0.286104	0.035*	0.6727 (17)
C2B	0.8979 (13)	0.2418 (14)	0.1659 (11)	0.0292 (11)	0.3273 (17)
H2B	0.982111	0.291811	0.161213	0.035*	0.3273 (17)
C3	0.83043 (16)	0.26481 (14)	0.26249 (13)	0.0229 (3)	
C4A	0.9131 (5)	0.2528 (5)	0.1785 (4)	0.0196 (7)	0.6727 (17)
H4A	0.998639	0.306140	0.183286	0.024*	0.6727 (17)
C4B	0.7015 (13)	0.1835 (11)	0.2382 (11)	0.0196 (7)	0.3273 (17)
H4B	0.634214	0.186979	0.287497	0.024*	0.3273 (17)
C5	0.87295 (17)	0.36183 (14)	0.37536 (13)	0.0244 (3)	
H5A	0.786386	0.394860	0.394322	0.029*	
H5B	0.937159	0.432803	0.362651	0.029*	
C6	0.94939 (15)	0.30218 (12)	0.47922 (12)	0.0195 (3)	
C7	0.99694 (15)	0.26354 (14)	0.76650 (13)	0.0219 (3)	
C8	0.91801 (15)	0.08293 (13)	0.61312 (13)	0.0211 (3)	
C9	0.99968 (17)	0.02374 (14)	0.71264 (13)	0.0255 (3)	
H9A	1.082011	-0.012463	0.688482	0.031*	
H9B	0.936797	-0.044373	0.731533	0.031*	
N1	0.87242 (13)	0.28734 (11)	0.56472 (11)	0.0205 (2)	
H1	0.784 (2)	0.2785 (16)	0.5452 (15)	0.023 (4)*	
N2	0.92535 (12)	0.21256 (11)	0.64903 (10)	0.0200 (2)	
O1	1.06854 (11)	0.26997 (10)	0.48825 (10)	0.0263 (2)	
O2	0.85315 (11)	0.03015 (10)	0.51434 (10)	0.0263 (2)	
S1A	0.84226 (13)	0.12988 (10)	0.06504 (10)	0.0260 (2)	0.6727 (17)
S1B	0.6811 (3)	0.0788 (3)	0.1107 (3)	0.0260 (2)	0.3273 (17)
S2	1.06254 (4)	0.14561 (4)	0.84299 (3)	0.02640 (9)	
S3	1.01734 (5)	0.41087 (4)	0.82790 (4)	0.03324 (10)	
C11A	0.4107 (4)	0.3665 (5)	0.8615 (4)	0.0348 (9)	0.7916 (19)
H11A	0.353131	0.424722	0.890676	0.042*	0.7916 (19)
C12A	0.3757 (4)	0.2893 (6)	0.7510 (5)	0.0260 (8)	0.7916 (19)
H12A	0.287724	0.288656	0.693747	0.031*	0.7916 (19)
C11B	0.6014 (12)	0.3318 (14)	0.9163 (10)	0.0348 (9)	0.2084 (19)
H11B	0.675966	0.365869	0.985263	0.042*	0.2084 (19)
C12B	0.6096 (19)	0.238 (3)	0.819 (2)	0.0260 (8)	0.2084 (19)

H12B	0.693246	0.198134	0.815566	0.031*	0.2084 (19)
C13	0.48263 (16)	0.20962 (13)	0.72904 (12)	0.0209 (3)	
C14A	0.5992 (5)	0.2286 (6)	0.8247 (5)	0.0279 (11)	0.7916 (19)
H14A	0.680976	0.184997	0.826702	0.033*	0.7916 (19)
C14B	0.3780 (19)	0.274 (3)	0.7503 (19)	0.0279 (11)	0.2084 (19)
H14B	0.285834	0.266998	0.697131	0.033*	0.2084 (19)
C15	0.46840 (16)	0.11790 (13)	0.61472 (12)	0.0216 (3)	
H15A	0.378555	0.059746	0.598778	0.026*	
H15B	0.550170	0.067657	0.623555	0.026*	
C16	0.46640 (14)	0.19004 (12)	0.51108 (12)	0.0173 (3)	
C17	0.31832 (14)	0.24127 (13)	0.24248 (12)	0.0192 (3)	
C18	0.33768 (14)	0.41284 (13)	0.40333 (13)	0.0190 (3)	
C19	0.33812 (17)	0.48314 (13)	0.29957 (13)	0.0247 (3)	
H19A	0.428495	0.540567	0.315257	0.030*	
H19B	0.256618	0.533625	0.288467	0.030*	
N11	0.33329 (13)	0.20086 (11)	0.44504 (10)	0.0173 (2)	
H11	0.261 (2)	0.1832 (16)	0.4689 (15)	0.025 (4)*	
N12	0.32383 (12)	0.28276 (10)	0.36245 (10)	0.0168 (2)	
O11	0.57399 (10)	0.23773 (10)	0.48702 (9)	0.0240 (2)	
O12	0.34760 (11)	0.45633 (9)	0.50671 (9)	0.0247 (2)	
S11A	0.58246 (9)	0.33791 (8)	0.93937 (6)	0.0371 (2)	0.7916 (19)
S11B	0.4286 (6)	0.3711 (5)	0.8833 (4)	0.0371 (2)	0.2084 (19)
S12	0.32221 (5)	0.36801 (4)	0.16587 (3)	0.02777 (9)	
S13	0.30889 (4)	0.09510 (3)	0.17993 (3)	0.02742 (9)	

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1A	0.037 (2)	0.057 (3)	0.038 (3)	0.0079 (19)	0.0078 (18)	0.012 (2)
C1B	0.037 (2)	0.057 (3)	0.038 (3)	0.0079 (19)	0.0078 (18)	0.012 (2)
C2A	0.0221 (16)	0.040 (3)	0.0266 (15)	0.0060 (14)	0.0066 (12)	0.0074 (15)
C2B	0.0221 (16)	0.040 (3)	0.0266 (15)	0.0060 (14)	0.0066 (12)	0.0074 (15)
C3	0.0264 (7)	0.0246 (7)	0.0184 (7)	0.0087 (6)	0.0044 (5)	0.0041 (5)
C4A	0.0234 (17)	0.0195 (14)	0.0152 (15)	0.0055 (11)	0.0024 (12)	0.0019 (10)
C4B	0.0234 (17)	0.0195 (14)	0.0152 (15)	0.0055 (11)	0.0024 (12)	0.0019 (10)
C5	0.0303 (8)	0.0230 (7)	0.0212 (7)	0.0101 (6)	0.0067 (6)	0.0028 (5)
C6	0.0185 (7)	0.0173 (6)	0.0204 (7)	0.0017 (5)	0.0028 (5)	-0.0019 (5)
C7	0.0181 (7)	0.0271 (7)	0.0210 (7)	0.0045 (6)	0.0049 (5)	0.0035 (5)
C8	0.0162 (6)	0.0232 (7)	0.0246 (7)	0.0002 (5)	0.0080 (5)	0.0026 (5)
C9	0.0300 (8)	0.0213 (7)	0.0251 (7)	0.0012 (6)	0.0061 (6)	0.0049 (6)
N1	0.0147 (6)	0.0262 (6)	0.0206 (6)	0.0072 (5)	0.0024 (5)	0.0033 (5)
N2	0.0177 (6)	0.0224 (6)	0.0195 (6)	0.0038 (5)	0.0034 (4)	0.0027 (4)
O1	0.0170 (5)	0.0314 (6)	0.0313 (6)	0.0057 (4)	0.0068 (4)	0.0042 (4)
O2	0.0220 (5)	0.0260 (5)	0.0268 (5)	-0.0008 (4)	0.0025 (4)	-0.0017 (4)
S1A	0.0297 (4)	0.0297 (4)	0.0182 (3)	0.0060 (3)	0.0044 (2)	0.0029 (2)
S1B	0.0297 (4)	0.0297 (4)	0.0182 (3)	0.0060 (3)	0.0044 (2)	0.0029 (2)
S2	0.0324 (2)	0.02659 (19)	0.02008 (18)	0.00490 (15)	0.00387 (14)	0.00602 (14)
S3	0.0405 (2)	0.02536 (19)	0.0278 (2)	0.01014 (17)	-0.00280 (17)	-0.00329 (15)

C11A	0.0280 (16)	0.0542 (18)	0.029 (2)	0.0119 (13)	0.0103 (14)	0.0206 (16)
C12A	0.0257 (11)	0.029 (2)	0.0267 (10)	0.0055 (10)	0.0130 (9)	0.0047 (11)
C11B	0.0280 (16)	0.0542 (18)	0.029 (2)	0.0119 (13)	0.0103 (14)	0.0206 (16)
C12B	0.0257 (11)	0.029 (2)	0.0267 (10)	0.0055 (10)	0.0130 (9)	0.0047 (11)
C13	0.0285 (7)	0.0181 (6)	0.0170 (6)	0.0015 (5)	0.0070 (5)	0.0039 (5)
C14A	0.0390 (17)	0.0221 (15)	0.0190 (12)	0.0073 (14)	-0.0020 (12)	0.0030 (11)
C14B	0.0390 (17)	0.0221 (15)	0.0190 (12)	0.0073 (14)	-0.0020 (12)	0.0030 (11)
C15	0.0268 (7)	0.0170 (6)	0.0185 (7)	0.0021 (5)	0.0009 (5)	0.0018 (5)
C16	0.0194 (6)	0.0150 (6)	0.0161 (6)	0.0041 (5)	0.0032 (5)	-0.0022 (5)
C17	0.0172 (6)	0.0217 (7)	0.0184 (6)	0.0033 (5)	0.0042 (5)	0.0017 (5)
C18	0.0144 (6)	0.0186 (6)	0.0237 (7)	0.0043 (5)	0.0048 (5)	0.0004 (5)
C19	0.0307 (8)	0.0192 (7)	0.0242 (7)	0.0064 (6)	0.0048 (6)	0.0041 (5)
N11	0.0161 (6)	0.0194 (6)	0.0174 (5)	0.0016 (4)	0.0053 (4)	0.0044 (4)
N12	0.0178 (5)	0.0164 (5)	0.0162 (5)	0.0035 (4)	0.0042 (4)	0.0016 (4)
O11	0.0159 (5)	0.0321 (6)	0.0250 (5)	0.0045 (4)	0.0059 (4)	0.0054 (4)
O12	0.0264 (5)	0.0228 (5)	0.0248 (5)	0.0022 (4)	0.0098 (4)	-0.0029 (4)
S11A	0.0573 (5)	0.0334 (3)	0.0176 (3)	0.0122 (3)	0.0034 (2)	-0.0020 (2)
S11B	0.0573 (5)	0.0334 (3)	0.0176 (3)	0.0122 (3)	0.0034 (2)	-0.0020 (2)
S12	0.0389 (2)	0.02616 (19)	0.01882 (18)	0.00436 (16)	0.00618 (15)	0.00631 (14)
S13	0.0352 (2)	0.02192 (18)	0.02263 (18)	0.00242 (15)	0.00702 (15)	-0.00483 (13)

Geometric parameters (Å, °)

C1A—H1A	0.9500	C5—C6	1.514 (2)
C1B—H1B	0.9500	C6—N1	1.3730 (18)
C1A—C2A	1.370 (8)	C6—O1	1.2141 (17)
C2A—H2A	0.9500	C7—N2	1.3878 (18)
C1B—C2B	1.395 (13)	C7—S2	1.7339 (15)
C2B—H2B	0.9500	C7—S3	1.6303 (15)
C2B—C3	1.410 (11)	C8—C9	1.494 (2)
C2A—C3	1.412 (6)	C8—N2	1.3988 (18)
C4A—H4A	0.9500	C8—O2	1.2065 (17)
C4B—H4B	0.9500	C9—H9A	0.9900
C4A—S1A	1.707 (4)	C9—H9B	0.9900
C1A—S1A	1.747 (7)	C9—S2	1.8102 (15)
C4B—S1B	1.690 (11)	N1—H1	0.825 (18)
C1B—S1B	1.672 (11)	N1—N2	1.3874 (16)
C11A—H11A	0.9500	C13—C14A	1.366 (4)
C11A—C12A	1.378 (6)	C13—C14B	1.323 (14)
C12A—H12A	0.9500	C13—C15	1.5086 (18)
C11B—H11B	0.9500	C15—H15A	0.9900
C11B—C12B	1.430 (16)	C15—H15B	0.9900
C12B—H12B	0.9500	C15—C16	1.5096 (19)
C12A—C13	1.442 (4)	C16—N11	1.3613 (17)
C12B—C13	1.395 (15)	C16—O11	1.2190 (17)
C14A—H14A	0.9500	C17—N12	1.3802 (17)
C14B—H14B	0.9500	C17—S12	1.7310 (14)
C11A—S11A	1.773 (4)	C17—S13	1.6326 (14)

C14A—S11A	1.694 (4)	C18—C19	1.501 (2)
C14B—S11B	1.680 (15)	C18—N12	1.4073 (17)
C11B—S11B	1.726 (12)	C18—O12	1.1982 (16)
C3—C4A	1.380 (5)	C19—H19A	0.9900
C3—C4B	1.407 (12)	C19—H19B	0.9900
C3—C5	1.509 (2)	C19—S12	1.8121 (15)
C5—H5A	0.9900	N11—H11	0.819 (18)
C5—H5B	0.9900	N11—N12	1.3797 (16)
C4A—S1A—C1A	92.8 (2)	C8—C9—H9B	110.3
S1A—C1A—H1A	125.5	C8—C9—S2	107.29 (10)
C2A—C1A—H1A	125.5	H9A—C9—H9B	108.5
S1B—C1B—H1B	125.0	S2—C9—H9A	110.3
C2B—C1B—H1B	125.0	S2—C9—H9B	110.3
C1A—C2A—H2A	122.6	C6—N1—H1	119.8 (12)
C1B—C2B—H2B	122.7	C6—N1—N2	116.15 (11)
C1A—C2A—C3	114.8 (4)	N2—N1—H1	112.4 (12)
C1B—C2B—C3	114.5 (8)	C7—N2—C8	118.28 (12)
S1A—C4A—H4A	124.2	N1—N2—C7	121.89 (12)
C1B—S1B—C4B	94.1 (5)	N1—N2—C8	119.59 (11)
S1B—C4B—H4B	124.1	C7—S2—C9	93.85 (7)
C2A—C1A—S1A	109.0 (4)	C14B—C13—C15	122.9 (6)
C2B—C1B—S1B	109.9 (7)	C13—C15—H15A	109.9
C14A—S11A—C11A	93.1 (2)	C3—C2A—H2A	122.6
C12A—C11A—H11A	126.1	C3—C2B—H2B	122.7
S11A—C11A—H11A	126.1	C3—C4A—H4A	124.2
C11A—C12A—H12A	122.6	C3—C4B—H4B	124.1
C14B—S11B—C11B	94.8 (6)	C13—C15—H15B	109.9
S11B—C11B—H11B	127.0	C3—C4A—S1A	111.5 (2)
C12B—C11B—H11B	127.0	C3—C4B—S1B	111.7 (6)
C11B—C12B—H12B	123.3	C13—C15—C16	108.99 (11)
C11A—C12A—C13	114.9 (3)	H15A—C15—H15B	108.3
S11A—C14A—H14A	123.6	C16—C15—H15A	109.9
S11B—C14B—H14B	124.3	C16—C15—H15B	109.9
C12A—C11A—S11A	107.8 (3)	N11—C16—C15	115.08 (12)
C12B—C11B—S11B	106.0 (8)	O11—C16—C15	123.93 (12)
C4A—C3—C2A	111.8 (2)	O11—C16—N11	120.98 (12)
C4B—C3—C2B	109.4 (6)	N12—C17—S12	109.87 (10)
C4A—C3—C5	122.36 (18)	N12—C17—S13	125.87 (11)
C4B—C3—C5	120.4 (4)	S13—C17—S12	124.26 (8)
C2A—C3—C5	125.5 (2)	N12—C18—C19	109.81 (11)
C2B—C3—C5	130.2 (4)	O12—C18—C19	127.34 (13)
C3—C5—H5A	109.8	O12—C18—N12	122.85 (13)
C3—C5—H5B	109.8	C18—C19—H19A	110.2
C14A—C13—C12A	111.3 (3)	C18—C19—H19B	110.2
C14B—C13—C12B	114.2 (8)	C18—C19—S12	107.46 (10)
C14A—C13—C15	124.3 (2)	H19A—C19—H19B	108.5
C12B—C13—C15	122.8 (6)	S12—C19—H19A	110.2

C12A—C13—C15	124.4 (2)	S12—C19—H19B	110.2
C3—C5—C6	109.31 (11)	C16—N11—H11	121.5 (12)
H5A—C5—H5B	108.3	C16—N11—N12	117.50 (11)
C6—C5—H5A	109.8	N12—N11—H11	117.0 (12)
C6—C5—H5B	109.8	C17—N12—C18	118.85 (11)
N1—C6—C5	114.18 (12)	N11—N12—C17	121.30 (11)
O1—C6—C5	123.98 (13)	N11—N12—C18	119.39 (11)
O1—C6—N1	121.84 (13)	C17—S12—C19	93.94 (7)
N2—C7—S2	109.78 (10)	C13—C12A—H12A	122.6
N2—C7—S3	126.68 (11)	C13—C12B—C11B	113.4 (10)
S3—C7—S2	123.53 (9)	C13—C12B—H12B	123.3
N2—C8—C9	110.62 (12)	C13—C14A—H14A	123.6
O2—C8—C9	126.72 (14)	C13—C14B—H14B	124.3
O2—C8—N2	122.66 (14)	C13—C14A—S11A	112.9 (3)
C8—C9—H9A	110.3	C13—C14B—S11B	111.5 (9)
C2B—C1B—S1B—C4B	0.0 (13)	N2—C8—C9—S2	4.36 (14)
C12A—C11A—S11A—C14A	0.2 (6)	O1—C6—N1—N2	-11.93 (19)
C2A—C1A—S1A—C4A	0.2 (5)	O2—C8—C9—S2	-175.56 (12)
C12B—C11B—S11B—C14B	-2 (2)	O2—C8—N2—C7	176.99 (13)
S1B—C1B—C2B—C3	3.4 (18)	O2—C8—N2—N1	-8.4 (2)
S1A—C1A—C2A—C3	1.4 (6)	S2—C7—N2—C8	-0.09 (15)
S11B—C11B—C12B—C13	2 (3)	S2—C7—N2—N1	-174.54 (10)
S11A—C11A—C12A—C13	0.0 (7)	S3—C7—N2—C8	-179.36 (11)
C1B—C2B—C3—C4B	-5.7 (17)	S3—C7—N2—N1	6.2 (2)
C1A—C2A—C3—C4A	-2.9 (7)	S3—C7—S2—C9	-178.31 (10)
C1A—C2A—C3—C5	-176.5 (4)	C12A—C13—C15—C16	65.3 (4)
C1B—C2B—C3—C5	177.4 (9)	C12B—C13—C15—C16	-106.2 (18)
C2A—C3—C5—C6	76.8 (3)	C14A—C13—C15—C16	-114.1 (4)
C4B—C3—C5—C6	84.8 (6)	C14B—C13—C15—C16	70.8 (19)
C4A—C3—C5—C6	-96.2 (4)	C13—C14B—S11B—C11B	2 (2)
C11B—C12B—C13—C14B	0 (3)	C13—C14A—S11A—C11A	-0.4 (5)
C11A—C12A—C13—C14A	-0.3 (6)	C13—C15—C16—N11	-96.18 (14)
C11A—C12A—C13—C15	-179.8 (4)	C13—C15—C16—O11	82.80 (16)
C11B—C12B—C13—C15	176.9 (15)	C15—C13—C14B—S11B	-178.4 (10)
C2A—C3—C4A—S1A	2.9 (6)	C15—C13—C14A—S11A	179.9 (2)
C2B—C3—C4B—S1B	5.5 (12)	C15—C16—N11—N12	169.47 (11)
C2B—C3—C5—C6	-98.6 (10)	C16—N11—N12—C17	95.69 (15)
C12A—C13—C14A—S11A	0.4 (5)	C16—N11—N12—C18	-76.45 (15)
C12B—C13—C14B—S11B	-1 (3)	C18—C19—S12—C17	-0.76 (11)
C3—C4A—S1A—C1A	-1.8 (4)	C19—C18—N12—C17	2.19 (17)
C3—C4B—S1B—C1B	-3.3 (10)	C19—C18—N12—N11	174.53 (11)
C3—C5—C6—N1	-110.03 (14)	N12—C17—S12—C19	1.91 (11)
C3—C5—C6—O1	70.25 (18)	N12—C18—C19—S12	-0.57 (14)
C5—C3—C4B—S1B	-177.2 (4)	O11—C16—N11—N12	-9.54 (18)
C5—C3—C4A—S1A	176.8 (2)	O12—C18—C19—S12	179.28 (12)
C5—C6—N1—N2	168.34 (12)	O12—C18—N12—C17	-177.67 (13)
C6—N1—N2—C7	104.36 (15)	O12—C18—N12—N11	-5.33 (19)

C6—N1—N2—C8	-70.01 (16)	S12—C17—N12—C18	-2.78 (15)
C8—C9—S2—C7	-3.86 (11)	S12—C17—N12—N11	-174.96 (10)
C9—C8—N2—C7	-2.94 (17)	S13—C17—N12—C18	177.43 (10)
C9—C8—N2—N1	171.64 (12)	S13—C17—N12—N11	5.25 (19)
N2—C7—S2—C9	2.39 (11)	S13—C17—S12—C19	-178.29 (10)

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

*Cg*1 and *Cg*2 are the centroids of the S1A/C1A–C4A and S11A/C11A–C14A rings, respectively.

<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—H1 \cdots O11	0.824 (19)	1.973 (19)	2.7923 (16)	173.1 (18)
N11—H11 \cdots O1 ⁱ	0.819 (19)	2.189 (19)	2.8436 (16)	137.1 (16)
N11—H11 \cdots O2 ⁱⁱ	0.819 (19)	2.519 (18)	3.0965 (16)	128.6 (15)
C5—H5A \cdots O12 ⁱⁱⁱ	0.99	2.46	3.3901 (19)	156
C9—H9A \cdots O2 ^{iv}	0.99	2.53	3.2443 (19)	129
C9—H9B \cdots S13 ⁱⁱ	0.99	2.81	3.6570 (17)	144
C15—H15A \cdots O2 ⁱⁱ	0.99	2.37	3.2862 (19)	154
C9—H9A \cdots <i>Cg</i> 1 ^{iv}	0.99	2.73	3.276 (3)	115
C19—H19A \cdots <i>Cg</i> 2 ⁱⁱⁱ	0.99	2.77	3.480 (2)	129

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