

A monoclinic polymorph of 1,2-bis[(1-methyl-1*H*-tetrazol-5-yl)sulfanyl]ethane (BMTTE)

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Keywords: crystal structure; polymorph; tetrazole-containing compounds; hydrogen bonding; π – π interactions.

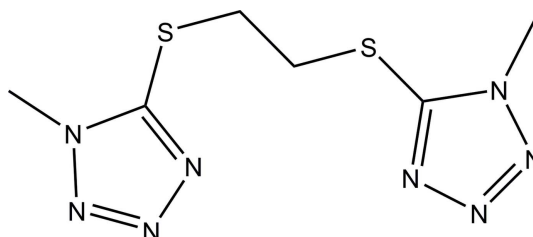
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The synthesis and crystal structure of a monoclinic ($P2_1/c$) polymorph of the title compound, $C_6H_{10}S_2N_8$, are reported. The molecule has pseudo-twofold rotational symmetry, with the tetrazole rings being inclined to one another by $5.50(6)^\circ$. In the crystal, molecules are linked by C–H \cdots N hydrogen bonds, forming chains propagating along [101] and enclosing $R_2^2(20)$ ring motifs. The chains are linked by offset π – π interactions involving the tetrazole rings [intercentroid distances vary from 3.3567(7) to 3.4227(7) Å], forming layers parallel to the *ac* plane. The crystal structure of the triclinic polymorph ($P\bar{1}$) has been described previously [Li *et al.* (2011). *Acta Cryst. E* **67**, o1669].

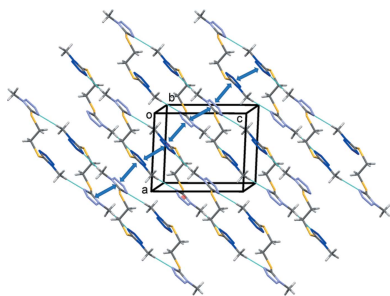
1. Chemical context

Organic compounds such as the title compound (BMTTE) are frequently used as flexible ligands for the preparation of coordination polymers (Wang *et al.*, 2010). A triclinic polymorph of the title compound has been described previously by Li *et al.*, (2011). Here we describe the spectroscopic characterization and crystal structure of a new monoclinic polymorph of BMTTE, obtained by recrystallization and slow evaporation from a solution in CH_3CN . Such compounds have been used in coordination chemistry (Zhao *et al.*, 2008) and in materials design (Wang *et al.*, 2009, 2010).



2. Structural commentary

The molecule structure of the title compound, Fig. 1, shows N–N and C–S bond distances and S–C–S and C–S–C–C torsion angles similar to the values observed in the triclinic form (Li *et al.*, 2011). As shown by the molecular overlap of the two polymorphs (Fig. 2), drawn with *Mercury* (Macrae *et al.*, 2008), there is only a slight difference in their geometry. The tetrazole rings (N1–N4/C1 and N5–N8/C4) are inclined to one another by $5.50(6)^\circ$ in the title polymorph and by $1.9(2)^\circ$ in the triclinic polymorph. While there are only small differences in the geometric parameters between the two



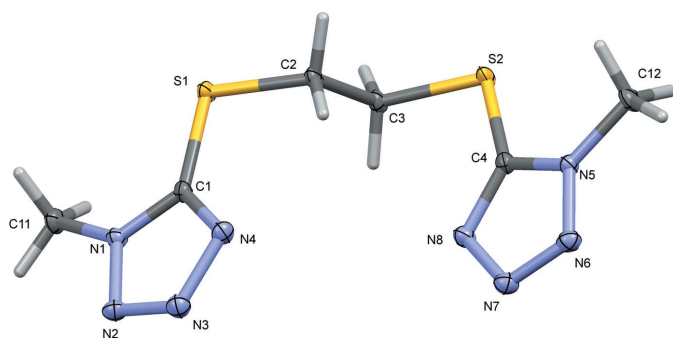


Figure 1
Molecular structure of the title compound, the monoclinic polymorph of BMTTE, with atom labelling. Displacement ellipsoids are drawn at the 50% probability level.

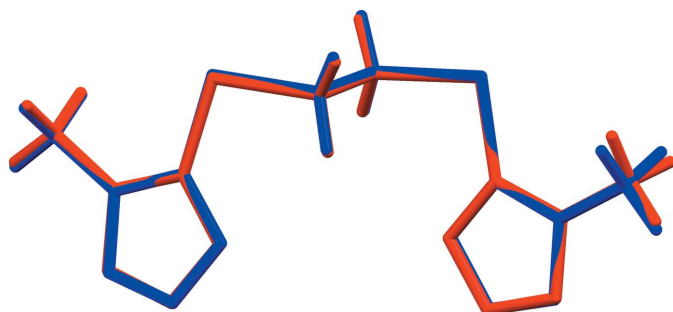


Figure 2
A molecular structure overlap (*Mercury*; Macrae *et al.*, 2008) of the title monoclinic polymorph of BMTTE (blue) and the triclinic polymorph (red; Li *et al.*, 2011).

polymorphic forms, they are enough to produce a different crystal packing.

3. Supramolecular features

In the crystal, molecules are linked by C–H···N hydrogen bonds, forming chains propagating along [101] and enclosing

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

<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>
C11–H11B···N8 ⁱ	0.98	2.39	3.3533 (13)	168
C12–H12B···N4 ⁱⁱ	0.98	2.36	3.3183 (13)	165

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

$R_2^2(20)$ ring motifs (Fig. 3 and Table 1). The chains are linked by offset π – π interactions involving the tetrazole rings, forming layers parallel to the *ac* plane, as shown in Fig. 4. The numerical details of these interactions are: $Cg1 \cdots Cg1^i = 3.365$ (1) Å, $\alpha = 0^\circ$, interplanar distance = 3.2056 (4) Å, offset = 1.024 Å; $Cg1 \cdots Cg2^{ii} = 3.423$ (1) Å, $\alpha = 5.5$ (1)°, interplanar distances = 3.278 (4) and 3.321 (4) Å, offset = 0.83 Å; and $Cg2 \cdots Cg2^{iii} = 3.4227$ (7) Å, $\alpha = 0^\circ$, interplanar distance = 3.1346 (4) Å, offset = 1.201 Å; *Cg1* and *Cg2* are the centroids of the tetrazole rings N1–N4/*C1* and N5–N8/*C4*, respectively; symmetry codes: (i) $-x + 1, -y, -z$; (ii) $x - 1, y, z$; (iii) $-x + 2, -y, -z + 1$.

As a result of these interactions, the molecules are packed very efficiently so that the Kitaigorodskii (1973) index is 72%. The crystal packing in the crystal of the triclinic polymorph is very similar, with a Kitaigorodskii index of 69% (*PLATON*; Spek, 2009).

4. Database survey

A search of the Cambridge Structural Database (CSD; version 5.38, last update May 2017; Groom *et al.*, 2016) for the skeleton of the title compound gave 11 hits. Apart from the crystal structure of the triclinic polymorph of the title compound (CSD refcode EVAWUU; Li *et al.*, 2011), and that of a diphenyl substituted compound, 1,2-bis(1-phenyl-1*H*-tetrazol-5-ylsulfanyl)ethane (IXAVUY; Wang *et al.*, 2004), all the others involve coordination compounds of BMTTE.

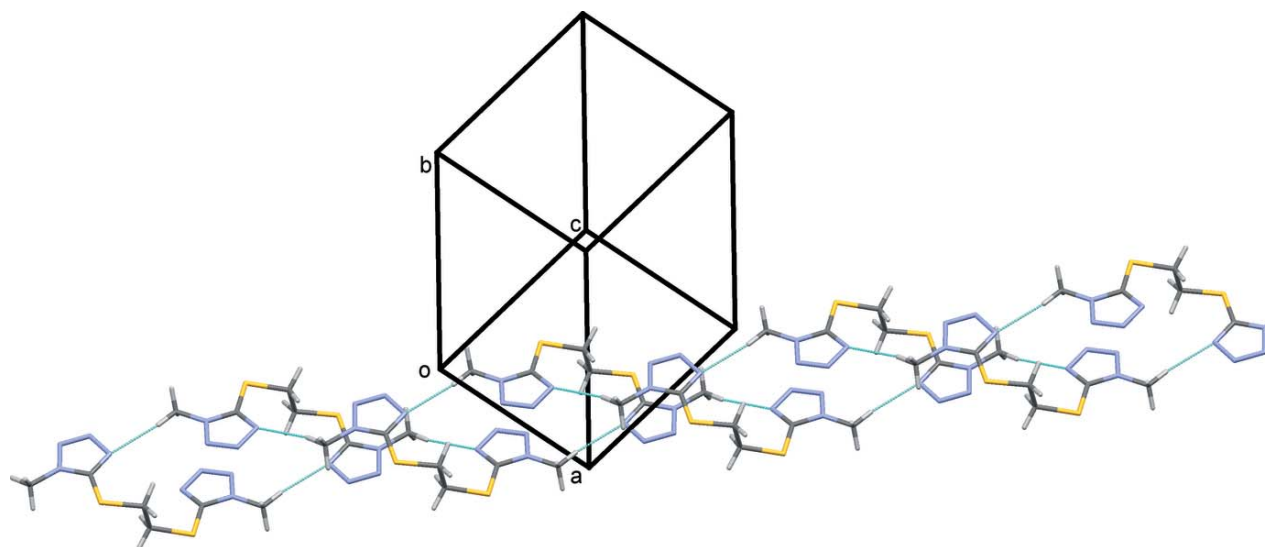


Figure 3
A partial view of the crystal packing of the title compound, showing details of the C–H···N hydrogen bonds (dashed lines, see Table 1).

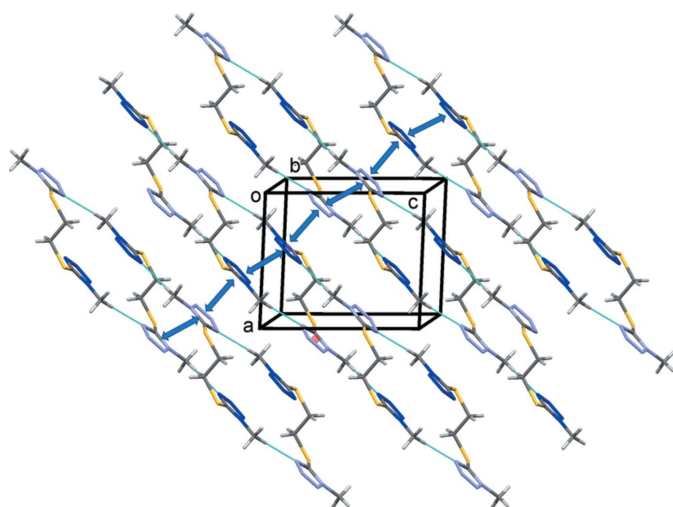


Figure 4
Crystal packing of the title compound, showing details of the C—H...N hydrogen bonds (dashed lines, see Table 1) and examples of the π – π interactions (blue double-headed arrows).

5. Synthesis and crystallization

The title compound, (BMTTE), was synthesized by a slightly modified version of the procedure described by Li *et al.* (2011). 5-Mercapto-1-methyltetrazole (9.29 g, 0.08 mol) was added to a solution of sodium hydroxide (3.26 g, 0.08 mol) in EtOH (110 ml). The mixture was stirred at room temperature for one day. Dichloroethane (3.2 ml, 0.04 mol) in 6 ml of EtOH was then added dropwise and the mixture was refluxed for 18 h. The resulting white solid was filtered, washed with H₂O and dried *in vacuo* (yield 88%; m.p. 417–419 K). Analysis calculated for C₆H₁₀S₂N₈: N 43.38, C 27.90, H 3.90%; Found: N 42.31, C 27.85, H 3.28%. IR (cm⁻¹): 1469*m*, 1442*m* (1408*m*, 1391*m*) ν (ring); 1276*m*, 1222*m*, ω (CH–CH₂); 1169*m*, δ (CH); 1144*m*, 1078*m*, 1026*m*, δ (ring); 728*m*, 716*m*, γ (CH); 698*s*, ν (C–S). ¹H NMR (400 MHz, dms_o-*d*₆) δ in ppm: 3.93 (*s*, 6H, H_b), 3.66 (*s*, 4H, H_a). MS–ESI: *m/z* (%) = 259 (100) [C₆H₁₀S₂N₈+H⁺]. Colourless prismatic crystals were obtained by slow evaporation of a solution in acetonitrile.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The C-bound H atoms were included in calculated positions and treated as riding: C–H = 0.98–0.99 Å with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C-methyl})$ and $1.2U_{\text{eq}}(\text{C})$ for other H atoms.

Funding information

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Table 2
Experimental details.

Crystal data	
Chemical formula	C ₆ H ₁₀ N ₈ S ₂
M_r	258.34
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	100
a, b, c (Å)	8.2456 (10), 13.7471 (17), 9.6878 (12)
β (°)	92.643 (4)
V (Å ³)	1097.0 (2)
Z	4
Radiation type	Mo $K\alpha$
μ (mm ⁻¹)	0.47
Crystal size (mm)	0.25 × 0.22 × 0.19
Data collection	
Diffractometer	Bruker D8 Venture Photon 100 CMOS
Absorption correction	Multi-scan (SADABS; Bruker, 2014)
$T_{\text{min}}, T_{\text{max}}$	0.697, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	23909, 2725, 2620
R_{int} ($\sin \theta/\lambda$) _{max} (Å ⁻¹)	0.024 0.668
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.022, 0.057, 1.08
No. of reflections	2725
No. of parameters	148
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å ⁻³)	0.36, –0.25

Computer programs: APEX3 (Bruker, 2014), SAINT (Bruker, 2014), SHELXS2014 (Sheldrick, 2008), Mercury (Macrae *et al.*, 2008), SHELXL2014 (Sheldrick, 2015), PLATON (Spek, 2009) and publCIF (Westrip, 2010).

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Computing details

Data collection: *APEX3* (Bruker, 2014); cell refinement: *SAINTE* (Bruker, 2014); data reduction: *SAINTE* (Bruker, 2014); program(s) used to solve structure: *SHELXS2014* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *SHELXL2014* (Sheldrick, 2015), *PLATON* (Spek, 2009) and *pubCIF* (Westrip, 2010).

1,2-Bis[(1-methyl-1*H*-tetrazol-5-yl)sulfanyl]ethane

Crystal data

$C_6H_{10}N_8S_2$

$M_r = 258.34$

Monoclinic, $P2_1/c$

$a = 8.2456$ (10) Å

$b = 13.7471$ (17) Å

$c = 9.6878$ (12) Å

$\beta = 92.643$ (4)°

$V = 1097.0$ (2) Å³

$Z = 4$

$F(000) = 536$

$D_x = 1.564$ Mg m⁻³

Melting point: 144 K

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

Cell parameters from 9507 reflections

$\theta = 2.5$ – 28.3 °

$\mu = 0.47$ mm⁻¹

$T = 100$ K

Prism, colourless

$0.25 \times 0.22 \times 0.19$ mm

Data collection

Bruker D8 Venture Photon 100 CMOS diffractometer

φ and ω scans

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

$T_{\min} = 0.697$, $T_{\max} = 0.746$

23909 measured reflections

2725 independent reflections

2620 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.024$

$\theta_{\max} = 28.3$ °, $\theta_{\min} = 2.5$ °

$h = -10 \rightarrow 11$

$k = -18 \rightarrow 18$

$l = -12 \rightarrow 12$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.022$

$wR(F^2) = 0.057$

$S = 1.08$

2725 reflections

148 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

$w = 1/[\sigma^2(F_o^2) + (0.0262P)^2 + 0.493P]$

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

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

$\Delta\rho_{\max} = 0.36$ e Å⁻³

$\Delta\rho_{\min} = -0.25$ e Å⁻³

Extinction correction: (SHELXL2014;
Sheldrick, 2015),
 $F_c^* = kF_c [1 + 0.001x F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.0376 (18)

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>	$U_{\text{iso}}^*/U_{\text{eq}}$
S1	0.46814 (3)	0.19617 (2)	0.21662 (2)	0.01218 (8)
S2	0.99483 (3)	0.22655 (2)	0.31188 (3)	0.01382 (8)
N1	0.32833 (10)	0.04027 (6)	0.08604 (8)	0.01158 (16)
N2	0.33462 (11)	-0.05843 (6)	0.08543 (9)	0.01445 (17)
N3	0.44707 (11)	-0.08272 (6)	0.17676 (9)	0.01511 (18)
N4	0.51615 (11)	-0.00275 (6)	0.23918 (9)	0.01383 (17)
N5	1.15565 (10)	0.07099 (6)	0.42528 (8)	0.01085 (16)
N6	1.16663 (10)	-0.02693 (6)	0.41075 (9)	0.01411 (17)
N7	1.06184 (11)	-0.05083 (6)	0.31273 (9)	0.01451 (17)
N8	0.98081 (11)	0.02894 (6)	0.26071 (9)	0.01352 (17)
C1	0.44014 (11)	0.07287 (7)	0.18059 (10)	0.01056 (18)
C2	0.66415 (11)	0.19192 (7)	0.31250 (10)	0.01208 (19)
H2A	0.6649	0.2392	0.3896	0.014*
H2B	0.6818	0.1262	0.3520	0.014*
C3	0.79982 (12)	0.21624 (7)	0.21671 (10)	0.01285 (19)
H3A	0.7747	0.2784	0.1687	0.015*
H3B	0.8064	0.1647	0.1458	0.015*
C4	1.04182 (11)	0.10381 (7)	0.33269 (10)	0.01087 (18)
C11	0.21707 (12)	0.09470 (7)	-0.00653 (10)	0.0147 (2)
H11A	0.1360	0.1277	0.0476	0.022*
H11B	0.1624	0.0499	-0.0721	0.022*
H11C	0.2781	0.1431	-0.0572	0.022*
C12	1.25381 (12)	0.12395 (7)	0.52931 (10)	0.0152 (2)
H12A	1.3335	0.1642	0.4838	0.023*
H12B	1.3105	0.0776	0.5914	0.023*
H12C	1.1834	0.1656	0.5827	0.023*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.01044 (12)	0.00922 (12)	0.01639 (13)	0.00092 (8)	-0.00455 (8)	0.00048 (8)
S2	0.01144 (13)	0.00868 (12)	0.02066 (14)	-0.00105 (8)	-0.00666 (9)	0.00047 (8)
N1	0.0121 (4)	0.0099 (4)	0.0125 (4)	0.0000 (3)	-0.0017 (3)	0.0000 (3)
N2	0.0164 (4)	0.0100 (4)	0.0170 (4)	0.0008 (3)	0.0007 (3)	-0.0005 (3)
N3	0.0153 (4)	0.0120 (4)	0.0178 (4)	0.0002 (3)	-0.0007 (3)	0.0006 (3)

N4	0.0140 (4)	0.0111 (4)	0.0162 (4)	0.0013 (3)	-0.0020 (3)	0.0019 (3)
N5	0.0110 (4)	0.0094 (4)	0.0119 (4)	0.0003 (3)	-0.0017 (3)	0.0007 (3)
N6	0.0156 (4)	0.0100 (4)	0.0168 (4)	0.0010 (3)	0.0019 (3)	0.0010 (3)
N7	0.0161 (4)	0.0115 (4)	0.0159 (4)	-0.0002 (3)	0.0007 (3)	-0.0003 (3)
N8	0.0150 (4)	0.0109 (4)	0.0145 (4)	-0.0013 (3)	-0.0014 (3)	-0.0010 (3)
C1	0.0091 (4)	0.0114 (4)	0.0111 (4)	0.0003 (3)	-0.0007 (3)	0.0007 (3)
C2	0.0107 (4)	0.0114 (4)	0.0136 (4)	0.0000 (3)	-0.0051 (3)	0.0002 (3)
C3	0.0108 (4)	0.0120 (4)	0.0153 (4)	-0.0006 (3)	-0.0048 (3)	0.0015 (3)
C4	0.0095 (4)	0.0115 (4)	0.0114 (4)	-0.0008 (3)	-0.0006 (3)	0.0004 (3)
C11	0.0137 (5)	0.0152 (5)	0.0144 (5)	0.0018 (4)	-0.0056 (4)	0.0008 (4)
C12	0.0152 (5)	0.0157 (5)	0.0140 (4)	-0.0022 (4)	-0.0062 (4)	-0.0003 (4)

Geometric parameters (Å, °)

S1—C1	1.7438 (10)	N7—N8	1.3681 (12)
S1—C2	1.8276 (10)	N8—C4	1.3290 (12)
S2—C4	1.7409 (10)	C2—C3	1.5232 (14)
S2—C3	1.8218 (10)	C2—H2A	0.9900
N1—C1	1.3461 (12)	C2—H2B	0.9900
N1—N2	1.3578 (12)	C3—H3A	0.9900
N1—C11	1.4594 (12)	C3—H3B	0.9900
N2—N3	1.2956 (12)	C11—H11A	0.9800
N3—N4	1.3663 (12)	C11—H11B	0.9800
N4—C1	1.3278 (12)	C11—H11C	0.9800
N5—C4	1.3459 (12)	C12—H12A	0.9800
N5—N6	1.3569 (12)	C12—H12B	0.9800
N5—C12	1.4580 (12)	C12—H12C	0.9800
N6—N7	1.2964 (12)		
C1—S1—C2	100.16 (4)	H2A—C2—H2B	108.2
C4—S2—C3	99.77 (5)	C2—C3—S2	111.39 (7)
C1—N1—N2	108.09 (8)	C2—C3—H3A	109.4
C1—N1—C11	129.71 (8)	S2—C3—H3A	109.4
N2—N1—C11	122.19 (8)	C2—C3—H3B	109.4
N3—N2—N1	106.31 (8)	S2—C3—H3B	109.4
N2—N3—N4	111.44 (8)	H3A—C3—H3B	108.0
C1—N4—N3	105.18 (8)	N8—C4—N5	108.99 (8)
C4—N5—N6	108.14 (8)	N8—C4—S2	127.81 (8)
C4—N5—C12	129.88 (8)	N5—C4—S2	123.14 (7)
N6—N5—C12	121.97 (8)	N1—C11—H11A	109.5
N7—N6—N5	106.38 (8)	N1—C11—H11B	109.5
N6—N7—N8	111.37 (8)	H11A—C11—H11B	109.5
C4—N8—N7	105.12 (8)	N1—C11—H11C	109.5
N4—C1—N1	108.98 (9)	H11A—C11—H11C	109.5
N4—C1—S1	128.32 (8)	H11B—C11—H11C	109.5
N1—C1—S1	122.69 (7)	N5—C12—H12A	109.5
C3—C2—S1	109.91 (7)	N5—C12—H12B	109.5
C3—C2—H2A	109.7	H12A—C12—H12B	109.5

S1—C2—H2A	109.7	N5—C12—H12C	109.5
C3—C2—H2B	109.7	H12A—C12—H12C	109.5
S1—C2—H2B	109.7	H12B—C12—H12C	109.5

Hydrogen-bond geometry (Å, °)

<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>
C11—H11 <i>B</i> \cdots N8 ⁱ	0.98	2.39	3.3533 (13)	168
C12—H12 <i>B</i> \cdots N4 ⁱⁱ	0.98	2.36	3.3183 (13)	165

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