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Crystal structure of benzyl 3-(3-methylphenyl)dithiocarbazate

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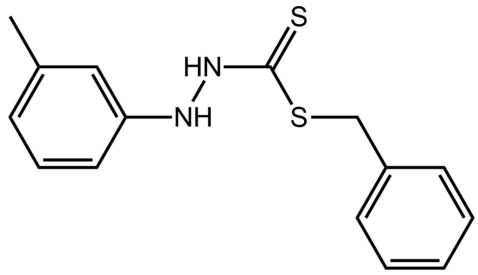
In the title compound, $C_{15}H_{16}N_2S_2$, the central CN_2S_2 residue is almost planar (r.m.s. deviation = 0.0354 Å) and forms dihedral angles of 56.02 (4) and 75.52 (4)° with the phenyl and tolyl rings, respectively; the dihedral angle between the aromatic rings is 81.72 (5)°. The conformation about the N—N bond is *gauche* [C—N—N—C = −117.48 (15)°]. Overall, the molecule has the shape of the letter *L*. In the crystal packing, supramolecular chains along the *a* axis are formed by N—H···S(thione) hydrogen bonds whereby the thione S atom accepts two such bonds. The hydrogen bonding leads to alternating edge-shared eight-membered $\{\cdots HNCS\}_2$ and 10-membered $\{\cdots HNNH\cdots S\}_2$ synthons. The chains are connected into layers by phenyl–tolyl C—H···π interactions; the layers stack along the *c* axis with no specific interactions between them.

Keywords: crystal structure; hydrogen bonding; C—H···π interactions; *S*-substituted dithiocarbazate.

CCDC reference: 1052727

1. Related literature

For background on the coordination chemistry of dithiocarbazate derivatives, see: Ravoof *et al.* (2010). For the structure of the 2-tolyl analogue, which is superimposable upon the title compound with the exception of the tolyl rings, see: Tayamon *et al.* (2012). For the synthesis, see: Tarafder *et al.* (2002).



2. Experimental

2.1. Crystal data

$C_{15}H_{16}N_2S_2$
M_r = 288.42
Monoclinic, $P2_1/n$
a = 5.9396 (1) Å
b = 10.3243 (2) Å
c = 23.5474 (5) Å
β = 96.952 (2)°
V = 1433.36 (5) Å^3
Z = 4
Cu $K\alpha$ radiation
μ = 3.25 mm^{-1}
T = 100 K
0.20 × 0.09 × 0.06 mm

2.2. Data collection

Oxford Diffraction Xcaliber Eos Gemini diffractometer
Absorption correction: multi-scan (*CrysAlis PRO*; Agilent, 2011)
T_{min} = 0.700, T_{max} = 1.000
18486 measured reflections
2784 independent reflections
2616 reflections with $I > 2\sigma(I)$
R_{int} = 0.022

2.3. Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.036
$wR(F^2)$ = 0.104
S = 1.01
2784 reflections
179 parameters
2 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.43 e Å^{-3}
$\Delta\rho_{min}$ = −0.31 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1*N*···S2^{i}	0.88 (1)	2.50 (2)	3.3581 (13)	167 (2)
N2—H2*N*···S2^{ii}	0.87 (1)	2.52 (1)	3.3819 (13)	167 (2)
C6—H6···*Cg*1^{iii}	0.95	2.61	3.5314 (19)	161

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

Data collection: *CrysAlis PRO* (Agilent, 2011); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis PRO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2015); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012), *QMOL* (Gans & Shalloway, 2001) and *DIAMOND* (Brandenburg, 2006); software used to prepare material for publication: *publCIF* (Westrip, 2010).

Acknowledgements

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Supporting information for this paper is available from the IUCr electronic archives (Reference: HB7378).

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supporting information

Acta Cryst. (2015). E**71**, o233–o234 [doi:10.1107/S2056989015004764]

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S1. Experimental

The compound was prepared according to Tarafder *et al.* (2002). *m*-Tolylhydrazine hydrochloride (0.05 mol) was added to a solution of potassium hydroxide (0.05 mol) in 95% ethanol (70 ml) with continual stirring. This mixture was cooled in an ice-bath until the temperature was about 268 K when the mixture was filtered to remove excess potassium chloride. Carbon disulfide (0.05 mol) was added drop-wise to the filtrate with vigorous stirring for about 1 h. The mixture was kept in the ice-salt bath while benzyl chloride (0.05 mol) was added drop-wise with vigorous stirring. Stirring was continued for 1 h after the complete addition of benzyl chloride. A pale-pink precipitate that was obtained was filtered and washed with cold ethanol. The product was dried in a desiccator and the filtrate was kept in freezer overnight. Pale-brown crystals were obtained from its filtrate. Yield 53.1%. *M*.pt: 416 K. Anal. Found (Calc.): C, 61.26 (62.46); H, 5.42 (5.59); N, 9.02 (9.71)%.

S2. Refinement

Carbon-bound H-atoms were placed in calculated positions (C—H = 0.95 to 0.99 Å) and were included in the refinement in the riding model approximation with U_{iso}(H) = 1.2–1.5U_{eq}(C). The N—H H atoms were refined with N—H = 0.88±0.01 Å, and with U_{iso}(H) = 1.2U_{eq}(N). Owing to poor agreement, the (0 0 2) reflection was omitted from the final cycles of refinement.

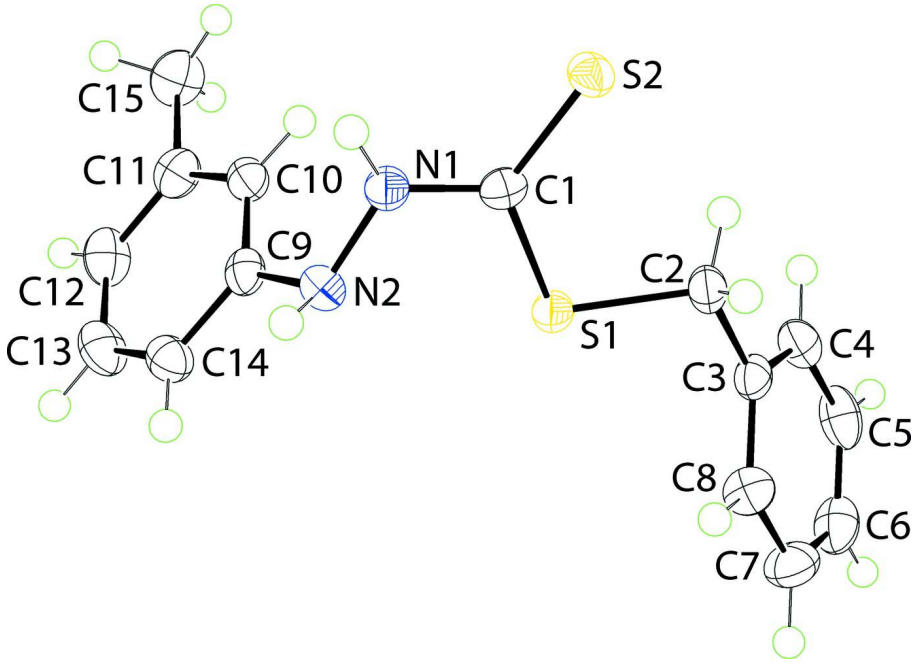

Figure 1

The molecular structure of the title compound showing displacement ellipsoids at the 70% probability level.

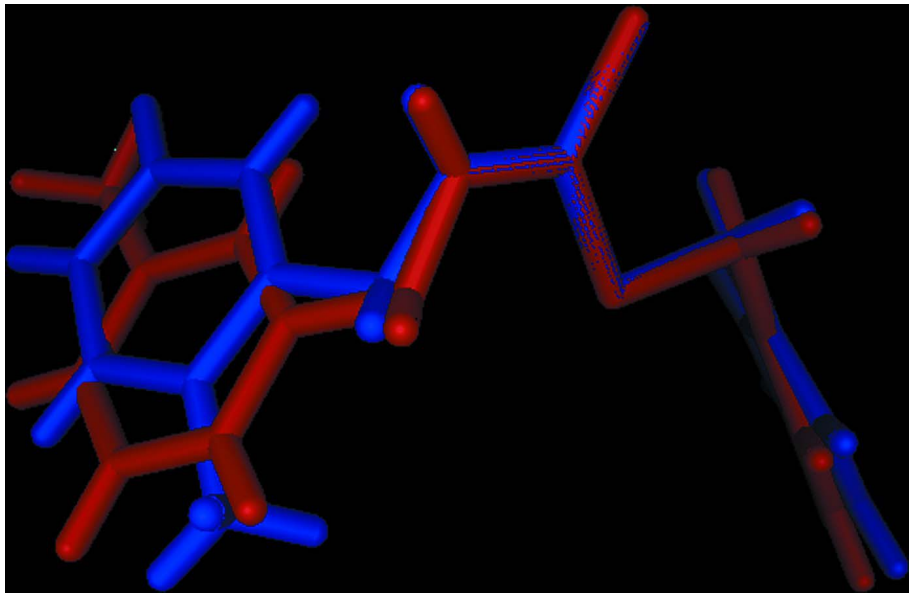

Figure 2

Superimposition of the title compound, shown in red, and the 2-tolyl analogue (blue). The molecules have been superimposed such that the CS_2 residues are overlapped.

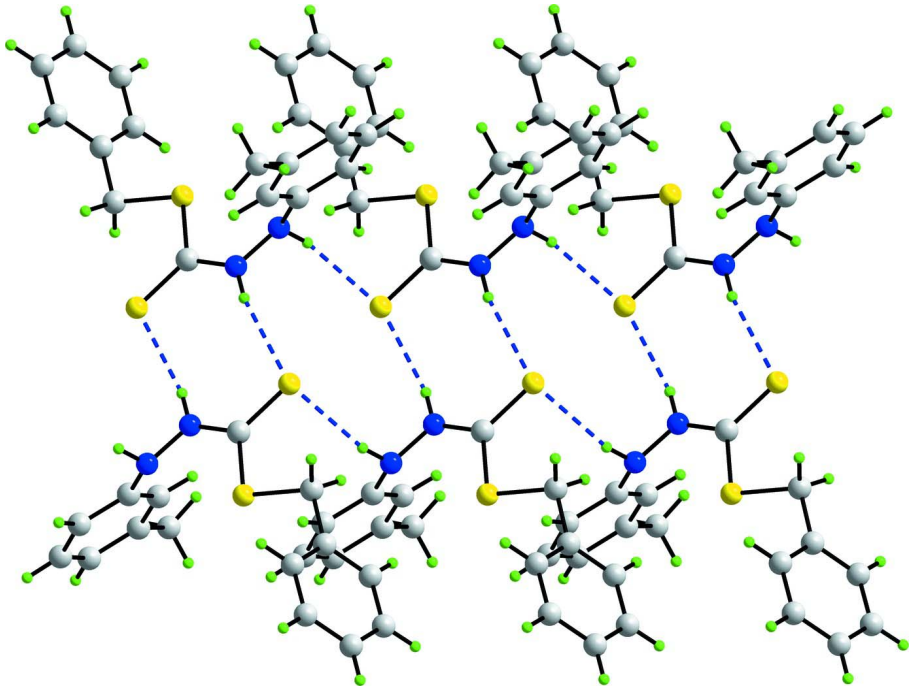

Figure 3

The supramolecular chain along the *a* axis sustained by N—H···S hydrogen bonding, shown as blue dashed lines.

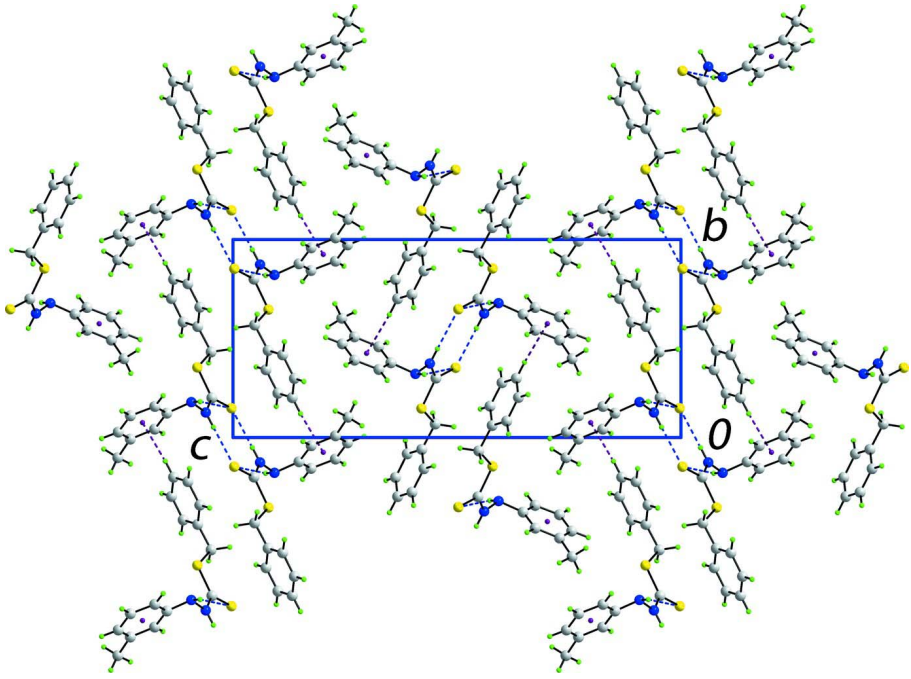

Figure 4

A view of the unit-cell contents in projection down the *a* axis. The N—H···S and C—H···π interactions are shown as blue and purple dashed lines, respectively.

1-Benzylsulfonyl-1,2,3,4-tetrahydroquinoline

Crystal data

$C_{15}H_{16}N_2S_2$
$M_r = 288.42$
Monoclinic, $P2_1/n$
$a = 5.9396$ (1) Å
$b = 10.3243$ (2) Å
$c = 23.5474$ (5) Å
$\beta = 96.952$ (2)°
$V = 1433.36$ (5) Å^3
$Z = 4$
$F(000) = 608$
$D_x = 1.337$ Mg m^{-3}
Cu $K\alpha$ radiation, $\lambda = 1.5418$ Å
Cell parameters from 9462 reflections
$\theta = 4.7$–$71.5°$
$\mu = 3.25$ mm^{-1}
$T = 100$ K
Prism, pale-brown
0.20 × 0.09 × 0.06 mm

Data collection

Oxford Diffraction Xcaliber Eos Gemini diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
Detector resolution: 16.1952 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (*CrysAlis PRO*; Agilent, 2011)
$T_{min} = 0.700$, $T_{max} = 1.000$
18486 measured reflections
2784 independent reflections
2616 reflections with $I > 2\sigma(I)$
$R_{int} = 0.022$
$\theta_{max} = 71.4°$, $\theta_{min} = 4.7°$
$h = -7 \rightarrow 7$
$k = -12 \rightarrow 12$
$l = -28 \rightarrow 28$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.036$
$wR(F^2) = 0.104$
$S = 1.01$
2784 reflections
179 parameters
2 restraints
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0719P)^2 + 0.7171P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.015$
$\Delta\rho_{max} = 0.43$ e Å^{-3}
$\Delta\rho_{min} = -0.31$ 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.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
S1	−0.02626 (6)	0.14613 (3)	0.57928 (2)	0.01811 (14)
S2	−0.27407 (6)	0.35220 (3)	0.50311 (2)	0.01879 (14)
N1	0.1325 (2)	0.37365 (13)	0.56063 (5)	0.0185 (3)
H1N	0.145 (3)	0.4481 (12)	0.5433 (8)	0.022*
N2	0.3251 (2)	0.32132 (13)	0.59271 (6)	0.0190 (3)
H2N	0.440 (2)	0.319 (2)	0.5728 (7)	0.023*
C1	−0.0490 (3)	0.29984 (14)	0.54689 (6)	0.0166 (3)
C2	−0.2885 (3)	0.06797 (15)	0.54854 (7)	0.0220 (3)
H2A	−0.4205	0.1231	0.5541	0.026*
H2B	−0.2867	0.0541	0.5070	0.026*

C3	−0.3054 (3)	−0.06035 (15)	0.57852 (6)	0.0183 (3)
C4	−0.4833 (3)	−0.08287 (17)	0.61097 (7)	0.0232 (3)
H4	−0.5904	−0.0163	0.6152	0.028*
C5	−0.5047 (3)	−0.20200 (18)	0.63711 (7)	0.0277 (4)
H5	−0.6282	−0.2171	0.6584	0.033*
C6	−0.3471 (3)	−0.29890 (17)	0.63237 (7)	0.0289 (4)
H6	−0.3606	−0.3799	0.6508	0.035*
C7	−0.1689 (3)	−0.27671 (16)	0.60040 (7)	0.0283 (4)
H7	−0.0606	−0.3430	0.5968	0.034*
C8	−0.1488 (3)	−0.15806 (16)	0.57376 (7)	0.0232 (4)
H8	−0.0263	−0.1437	0.5520	0.028*
C9	0.3914 (3)	0.37731 (15)	0.64746 (6)	0.0182 (3)
C10	0.2516 (3)	0.45821 (15)	0.67466 (6)	0.0194 (3)
H10	0.1050	0.4796	0.6563	0.023*
C11	0.3250 (3)	0.50851 (16)	0.72891 (7)	0.0231 (3)
C12	0.5383 (3)	0.47294 (18)	0.75585 (7)	0.0266 (4)
H12	0.5897	0.5053	0.7929	0.032*
C13	0.6756 (3)	0.39062 (18)	0.72868 (7)	0.0270 (4)
H13	0.8197	0.3662	0.7476	0.032*
C14	0.6050 (3)	0.34342 (16)	0.67428 (7)	0.0220 (3)
H14	0.7014	0.2886	0.6556	0.026*
C15	0.1791 (3)	0.60228 (19)	0.75688 (8)	0.0304 (4)
H15A	0.1134	0.5586	0.7879	0.046*
H15B	0.0571	0.6339	0.7285	0.046*
H15C	0.2718	0.6756	0.7724	0.046*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0189 (2)	0.0149 (2)	0.0195 (2)	−0.00064 (12)	−0.00198 (15)	0.00260 (13)
S2	0.0174 (2)	0.0191 (2)	0.0192 (2)	0.00001 (13)	−0.00053 (15)	0.00490 (13)
N1	0.0193 (6)	0.0165 (6)	0.0189 (6)	−0.0008 (5)	−0.0012 (5)	0.0036 (5)
N2	0.0166 (6)	0.0212 (7)	0.0189 (6)	0.0010 (5)	0.0009 (5)	0.0006 (5)
C1	0.0204 (7)	0.0157 (7)	0.0141 (6)	0.0019 (6)	0.0037 (5)	−0.0002 (5)
C2	0.0194 (7)	0.0187 (8)	0.0259 (8)	−0.0037 (6)	−0.0055 (6)	0.0019 (6)
C3	0.0202 (7)	0.0177 (7)	0.0160 (7)	−0.0026 (6)	−0.0020 (6)	−0.0007 (6)
C4	0.0188 (7)	0.0288 (9)	0.0214 (7)	0.0000 (6)	−0.0001 (6)	−0.0016 (7)
C5	0.0227 (8)	0.0404 (10)	0.0197 (8)	−0.0116 (7)	0.0013 (6)	0.0046 (7)
C6	0.0350 (9)	0.0233 (9)	0.0265 (8)	−0.0089 (7)	−0.0046 (7)	0.0073 (7)
C7	0.0344 (9)	0.0183 (8)	0.0316 (9)	0.0033 (7)	0.0019 (7)	0.0023 (7)
C8	0.0256 (8)	0.0218 (8)	0.0228 (8)	0.0002 (6)	0.0055 (6)	0.0010 (6)
C9	0.0191 (7)	0.0178 (7)	0.0174 (7)	−0.0044 (6)	0.0009 (6)	0.0038 (6)
C10	0.0180 (7)	0.0192 (7)	0.0206 (7)	−0.0017 (6)	0.0012 (6)	0.0040 (6)
C11	0.0266 (8)	0.0224 (8)	0.0211 (7)	−0.0035 (6)	0.0063 (6)	0.0019 (6)
C12	0.0288 (8)	0.0333 (9)	0.0169 (7)	−0.0065 (7)	−0.0006 (6)	0.0005 (7)
C13	0.0217 (8)	0.0344 (9)	0.0233 (8)	−0.0016 (7)	−0.0036 (6)	0.0057 (7)
C14	0.0194 (8)	0.0235 (8)	0.0230 (8)	0.0006 (6)	0.0021 (6)	0.0041 (6)
C15	0.0353 (9)	0.0319 (10)	0.0248 (8)	−0.0013 (8)	0.0070 (7)	−0.0059 (7)

Geometric parameters (Å, º)

S1—C1	1.7588 (15)	C6—H6	0.9500
S1—C2	1.8245 (16)	C7—C8	1.388 (2)
S2—C1	1.6761 (15)	C7—H7	0.9500
N1—C1	1.328 (2)	C8—H8	0.9500
N1—N2	1.4007 (18)	C9—C10	1.388 (2)
N1—H1N	0.878 (9)	C9—C14	1.392 (2)
N2—C9	1.424 (2)	C10—C11	1.399 (2)
N2—H2N	0.875 (9)	C10—H10	0.9500
C2—C3	1.510 (2)	C11—C12	1.396 (2)
C2—H2A	0.9900	C11—C15	1.503 (2)
C2—H2B	0.9900	C12—C13	1.386 (3)
C3—C8	1.386 (2)	C12—H12	0.9500
C3—C4	1.397 (2)	C13—C14	1.387 (2)
C4—C5	1.388 (3)	C13—H13	0.9500
C4—H4	0.9500	C14—H14	0.9500
C5—C6	1.384 (3)	C15—H15A	0.9800
C5—H5	0.9500	C15—H15B	0.9800
C6—C7	1.390 (3)	C15—H15C	0.9800
C1—S1—C2	102.12 (7)	C8—C7—H7	119.9
C1—N1—N2	119.73 (13)	C6—C7—H7	119.9
C1—N1—H1N	120.1 (13)	C3—C8—C7	120.68 (15)
N2—N1—H1N	118.6 (13)	C3—C8—H8	119.7
N1—N2—C9	116.74 (13)	C7—C8—H8	119.7
N1—N2—H2N	111.2 (13)	C10—C9—C14	120.35 (15)
C9—N2—H2N	110.3 (13)	C10—C9—N2	123.14 (14)
N1—C1—S2	121.90 (11)	C14—C9—N2	116.47 (14)
N1—C1—S1	113.26 (11)	C9—C10—C11	120.48 (14)
S2—C1—S1	124.84 (9)	C9—C10—H10	119.8
C3—C2—S1	107.71 (10)	C11—C10—H10	119.8
C3—C2—H2A	110.2	C12—C11—C10	118.85 (15)
S1—C2—H2A	110.2	C12—C11—C15	120.66 (15)
C3—C2—H2B	110.2	C10—C11—C15	120.46 (15)
S1—C2—H2B	110.2	C13—C12—C11	120.25 (15)
H2A—C2—H2B	108.5	C13—C12—H12	119.9
C8—C3—C4	118.88 (15)	C11—C12—H12	119.9
C8—C3—C2	121.17 (14)	C12—C13—C14	120.85 (15)
C4—C3—C2	119.94 (14)	C12—C13—H13	119.6
C5—C4—C3	120.39 (16)	C14—C13—H13	119.6
C5—C4—H4	119.8	C13—C14—C9	119.18 (16)
C3—C4—H4	119.8	C13—C14—H14	120.4
C6—C5—C4	120.40 (15)	C9—C14—H14	120.4
C6—C5—H5	119.8	C11—C15—H15A	109.5
C4—C5—H5	119.8	C11—C15—H15B	109.5
C5—C6—C7	119.42 (15)	H15A—C15—H15B	109.5
C5—C6—H6	120.3	C11—C15—H15C	109.5

C7—C6—H6	120.3	H15A—C15—H15C	109.5
C8—C7—C6	120.22 (16)	H15B—C15—H15C	109.5
C1—N1—N2—C9	−117.48 (15)	C2—C3—C8—C7	−178.47 (15)
N2—N1—C1—S2	−173.66 (10)	C6—C7—C8—C3	−0.1 (3)
N2—N1—C1—S1	6.62 (17)	N1—N2—C9—C10	14.4 (2)
C2—S1—C1—N1	−176.50 (11)	N1—N2—C9—C14	−167.76 (13)
C2—S1—C1—S2	3.79 (12)	C14—C9—C10—C11	1.1 (2)
C1—S1—C2—C3	−173.00 (11)	N2—C9—C10—C11	178.89 (14)
S1—C2—C3—C8	−64.36 (17)	C9—C10—C11—C12	−1.8 (2)
S1—C2—C3—C4	116.71 (14)	C9—C10—C11—C15	176.39 (15)
C8—C3—C4—C5	−1.1 (2)	C10—C11—C12—C13	0.9 (2)
C2—C3—C4—C5	177.82 (14)	C15—C11—C12—C13	−177.29 (16)
C3—C4—C5—C6	1.4 (2)	C11—C12—C13—C14	0.7 (3)
C4—C5—C6—C7	−1.0 (3)	C12—C13—C14—C9	−1.4 (3)
C5—C6—C7—C8	0.4 (3)	C10—C9—C14—C13	0.5 (2)
C4—C3—C8—C7	0.5 (2)	N2—C9—C14—C13	−177.39 (14)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*N*···S2^{i}	0.88 (1)	2.50 (2)	3.3581 (13)	167 (2)
N2—H2*N*···S2^{ii}	0.87 (1)	2.52 (1)	3.3819 (13)	167 (2)
C6—H6···*Cg*1^{iii}	0.95	2.61	3.5314 (19)	161

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