



Crystal structure of 4-methylbenzyl *N'*-(thiophen-2-yl)methylidene]-hydrazinecarbodithioate

Syahirah binti Ramli,^{a*} Thahira Begum S. A. Ravoof,^{a*} Mohamed Ibrahim Mohamed Tahir^a and Edward R. T. Tiekink^b

^aDepartment of Chemistry, Universiti Putra Malaysia, 43400 Serdang, Malaysia, and

^bDepartment of Chemistry, University of Malaya, 50603 Kuala Lumpur, Malaysia.

*Correspondence e-mail: thahira@upm.edu.my

Received 3 June 2015; accepted 8 June 2015

Edited by W. T. A. Harrison, University of Aberdeen, Scotland

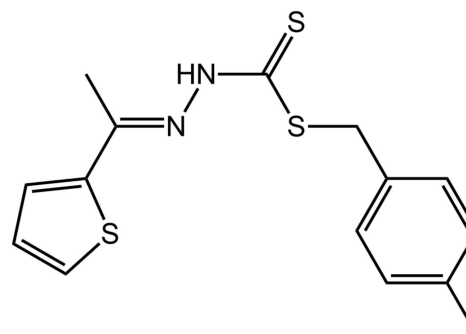
In the title compound, C₁₅H₁₆N₂S₃ {systematic name: [(((4-methylphenyl)methyl)sulfanyl)methanethiyl)amino][1-(thiophen-2-yl)ethylidene]amine}, the central CN₂S₂ residue is almost planar (r.m.s. deviation = 0.0061 Å) and forms dihedral angles of 7.39 (10) and 64.91 (5)° with the thienyl and *p*-tolyl rings, respectively; the dihedral angle between these rings is 57.52 (6)°. The non-thione S atoms are *syn*, and with respect to the thione S atom, the benzyl group is *anti*. In the crystal, centrosymmetrically related molecules self-associate *via* eight-membered {···HNCS₂}₂ synthons. The dimeric aggregates stack along the *a* axis and are consolidated into a three-dimensional architecture *via* methyl-C—H···π(benzene) and benzene-C—H···π(thienyl) interactions.

Keywords: crystal structure; hydrogen bonding; dithiocarbamate; C—H···π interactions.

CCDC reference: 1405284

1. Related literature

For the structure of the parent compound, in which the benzyl residue is *syn* to the thione S atom, see: Chan *et al.* (2003). For the synthesis, see: Tarafder *et al.* (2002).



2. Experimental

2.1. Crystal data

C₁₅H₁₆N₂S₃

M_r = 320.48

Monoclinic, *P*2₁/*c*

a = 5.6956 (4) Å

b = 14.3424 (9) Å

c = 18.9255 (11) Å

β = 90.263 (5)°

V = 1545.98 (17) Å³

Z = 4

Cu Kα radiation

μ = 4.30 mm⁻¹

T = 150 K

0.15 × 0.10 × 0.06 mm

2.2. Data collection

Oxford Diffraction Xcaliber Eos

Gemini diffractometer

Absorption correction: multi-scan

(*CrysAlis PRO*; Agilent, 2011)

T_{min} = 0.774, *T_{max}* = 1.000

8463 measured reflections

2830 independent reflections

2506 reflections with *I* > 2σ(*I*)

R_{int} = 0.023

2.3. Refinement

R[*F*² > 2σ(*F*²)] = 0.039

wR(*F*²) = 0.109

S = 1.06

2830 reflections

186 parameters

1 restraint

H atoms treated by a mixture of independent and constrained refinement

Δρ_{max} = 0.49 e Å⁻³

Δρ_{min} = -0.33 e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

*Cg*1 and *Cg*2 are the centroids of the S3,C3–C6 and C8–C13 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—H1N···S2 ⁱ	0.87 (2)	2.57 (2)	3.4433 (18)	176 (3)
C2'—H2'2···Cg2 ⁱⁱ	0.98	2.85	3.616 (3)	138
C12—H12···Cg1 ⁱⁱⁱ	0.95	2.89	3.560 (2)	130

Symmetry codes: (i) $-x + 1, -y + 2, -z + 1$; (ii) $x - 1, -y + \frac{1}{2}, z - \frac{1}{2}$; (iii) $-x + 1, -y + 1, -z + 1$.

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) and *DIAMOND* (Brandenburg, 2006); software used to prepare material for publication: *pubCIF* (Westrip, 2010).

Acknowledgements

The research was funded by Universiti Putra Malaysia (UPM) under Research University Grant Schemes (RUGS No. 9419400), the Fundamental Research Grant Scheme (FRGS No. 5524425) and the Science Fund (Science Fund No. 06-01-04-SF810). SR thanks the UPM for the award of a Graduate Research Fellowship.

Supporting information for this paper is available from the IUCr electronic archives (Reference: HB7439).

References

- Agilent (2011). *CrysAlis PRO*. Agilent Technologies, Yarnton, England.
- Brandenburg, K. (2006). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.
- Chan, M.-H. E., Crouse, K. A., Tarafder, M. T. H. & Yamin, B. M. (2003). *Acta Cryst.* **E59**, o628–o629.
- Farrugia, L. J. (2012). *J. Appl. Cryst.* **45**, 849–854.
- Sheldrick, G. M. (2015). *Acta Cryst.* **C71**, 3–8.
- Tarafder, M. T. H., Khoo, T.-J., Crouse, K. A., Ali, A. M., Yamin, B. M. & Fun, H.-K. (2002). *Polyhedron*, **21**, 2691–2698.
- Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.

supporting information

Acta Cryst. (2015). E71, o475–o476 [doi:10.1107/S205698901501107X]

Crystal structure of 4-methylbenzyl *N'*-[(thiophen-2-yl)methylidene]hydrazinecarbodithioate

Syahirah binti Ramli, Thahira Begum S. A. Ravoof, Mohamed Ibrahim Mohamed Tahir and Edward R. T. Tiekink

S1. Experimental

The title compound was prepared as per a reported procedure (Tarafder *et al.*, 2002). The light-yellow precipitate formed was filtered off and recrystallized from its acetonitrile solution as yellow prisms. Yield 56%; *M*.pt: 175–177 °C. Anal. Calcd for C₁₅H₁₆N₂S₃: C, 56.21; H, 5.03; N, 8.74. Found: C, 55.97; H, 4.96; N, 8.10. IR (cm⁻¹, FT—IR): 3143 w, 1511 m, 1060 m, 924 s. ¹H-NMR: (DMSO-*d*₆, p.p.m.) δ: 12.42 (s, 1H, NH), 7.24–7.55 (multiplet, 4H, Ar-H), 7.03–7.10 (multiplet, 3H, thiophene-H), 4.37 (s, 2H, –SCH₂), 2.24, 2.36 (s, 6H, –CH₃), 13 C-NMR:(DMSO-*d*₆, p.p.m.) δ: 197.98 (C=S), 159.15 (C=N), 129.32–142.86 (Ar-C), 128.39–129.90 (thiophene-C), 38.23 (SCH₂), 15.58, 21.24 (CH₃).

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 $U_{\text{iso}}(\text{H}) = 1.2\text{--}1.5U_{\text{eq}}(\text{C})$. The N–H atom was refined with N–H = 0.88±0.01 Å, and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{N})$.

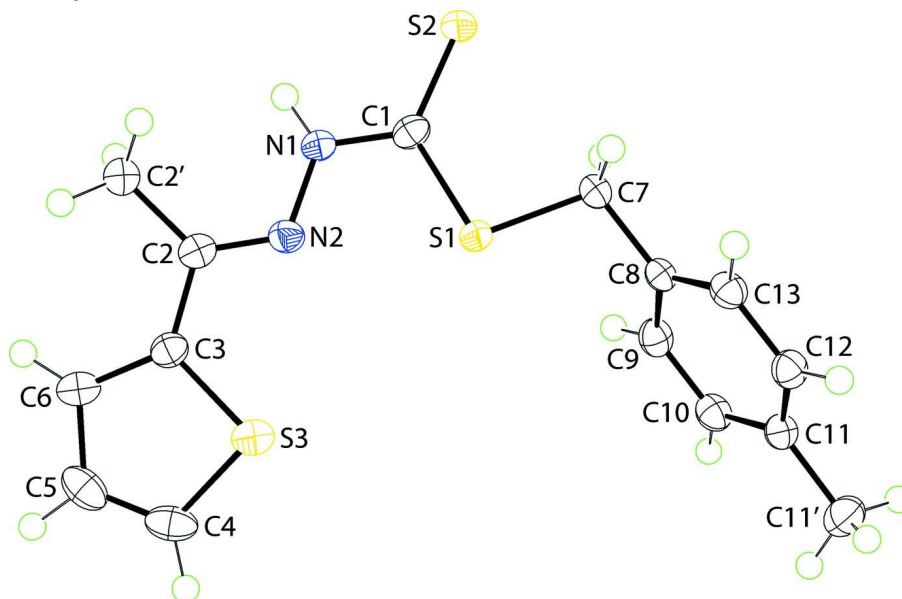
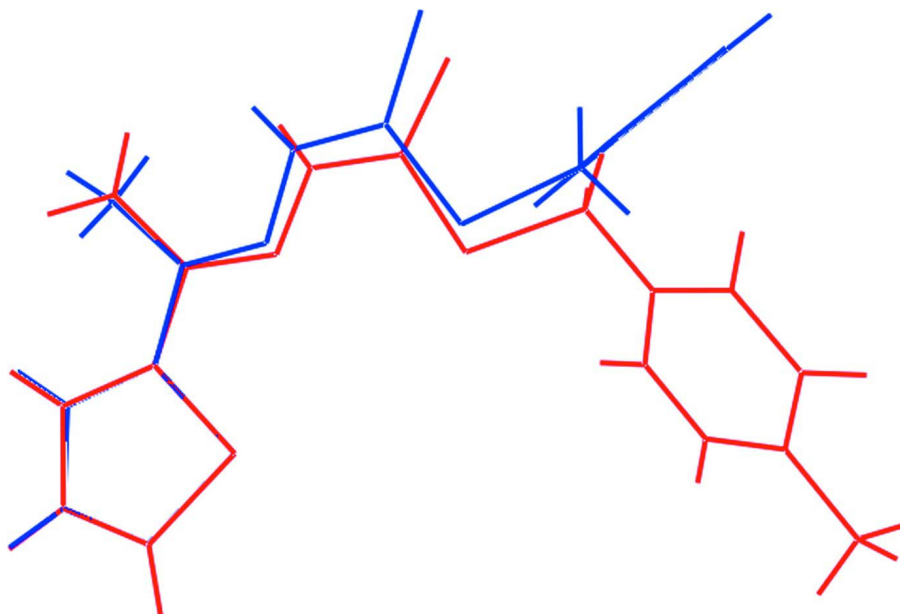
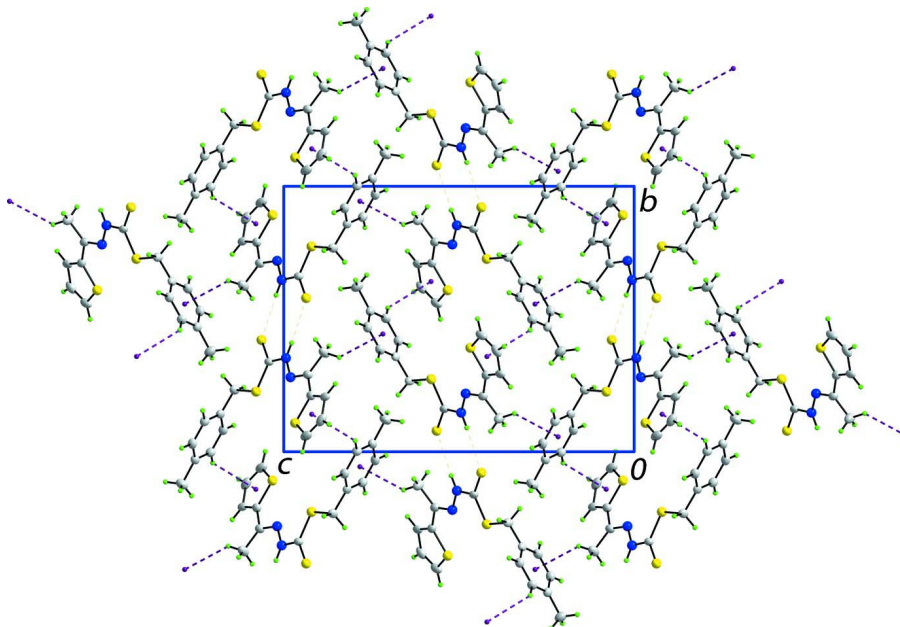


Figure 1

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

**Figure 2**

Overlay diagram of the title compound (red image) with the parent compound (blue). The molecules have been overlapped so that the thienyl residues are coincident.

**Figure 3**

A view of the unit-cell contents in projection down the *a* axis. The N—H \cdots S (orange) and C—H \cdots π (purple) interactions are shown as dashed lines.

[[{(4-Methylphenyl)methyl}sulfanyl]methanethiyl)amino][1-(thiophen-2-yl)ethylidene]amine

Crystal data

C₁₅H₁₆N₂S₃ $M_r = 320.48$ Monoclinic, $P2_1/c$ $a = 5.6956$ (4) Å $b = 14.3424$ (9) Å $c = 18.9255$ (11) Å $\beta = 90.263$ (5)° $V = 1545.98$ (17) Å³ $Z = 4$ $F(000) = 672$ $D_x = 1.377$ Mg m⁻³Cu $K\alpha$ radiation, $\lambda = 1.54182$ Å

Cell parameters from 3915 reflections

 $\theta = 3.1$ – 71.3 ° $\mu = 4.30$ mm⁻¹ $T = 150$ K

Prism, yellow

 $0.15 \times 0.10 \times 0.06$ 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)

 $T_{\min} = 0.774$, $T_{\max} = 1.000$

8463 measured reflections

2830 independent reflections

2506 reflections with $I > 2\sigma(I)$ $R_{\text{int}} = 0.023$ $\theta_{\max} = 71.3$ °, $\theta_{\min} = 3.9$ ° $h = -6$ → 6 $k = -17$ → 17 $l = -16$ → 22

Refinement

Refinement on F^2

Least-squares matrix: full

 $R[F^2 > 2\sigma(F^2)] = 0.039$ $wR(F^2) = 0.109$ $S = 1.06$

2830 reflections

186 parameters

1 restraint

Hydrogen site location: mixed

H atoms treated by a mixture of independent and constrained refinement

 $w = 1/[\sigma^2(F_o^2) + (0.0667P)^2 + 0.9619P]$ where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\max} = 0.001$ $\Delta\rho_{\max} = 0.49$ e Å⁻³ $\Delta\rho_{\min} = -0.33$ 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 (Å²)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
S1	0.51174 (9)	0.72659 (3)	0.42082 (3)	0.01620 (16)
S2	0.71326 (10)	0.92093 (3)	0.43627 (3)	0.02009 (17)
S3	-0.06660 (10)	0.60844 (4)	0.53247 (3)	0.02183 (17)
N1	0.3513 (3)	0.85288 (12)	0.50603 (10)	0.0179 (4)
H1N	0.339 (5)	0.9097 (9)	0.5222 (13)	0.021*
N2	0.1971 (3)	0.78079 (12)	0.51907 (10)	0.0170 (4)
C1	0.5185 (4)	0.83886 (14)	0.45784 (12)	0.0171 (4)
C2	0.0454 (4)	0.79016 (15)	0.56846 (12)	0.0179 (5)
C2'	0.0181 (5)	0.87383 (16)	0.61556 (13)	0.0258 (5)
H2'1	0.1735	0.8977	0.6287	0.039*

H2'2	-0.0675	0.8559	0.6583	0.039*
H2'3	-0.0696	0.9224	0.5904	0.039*
C3	-0.1146 (4)	0.71133 (15)	0.57733 (12)	0.0174 (4)
C4	-0.3185 (4)	0.56050 (16)	0.56418 (13)	0.0237 (5)
H4	-0.3703	0.4993	0.5530	0.028*
C5	-0.4368 (4)	0.61936 (17)	0.60721 (13)	0.0243 (5)
H5	-0.5818	0.6033	0.6286	0.029*
C6	-0.3258 (4)	0.70718 (14)	0.61767 (12)	0.0175 (5)
H6	-0.3834	0.7557	0.6470	0.021*
C7	0.7561 (4)	0.73279 (15)	0.35948 (12)	0.0184 (5)
H7A	0.7341	0.7856	0.3265	0.022*
H7B	0.9052	0.7421	0.3856	0.022*
C8	0.7625 (4)	0.64185 (14)	0.31920 (11)	0.0165 (4)
C9	0.5788 (4)	0.61510 (15)	0.27450 (12)	0.0186 (5)
H9	0.4473	0.6551	0.2684	0.022*
C10	0.5867 (4)	0.53072 (15)	0.23898 (12)	0.0188 (5)
H10	0.4602	0.5136	0.2087	0.023*
C11	0.7773 (4)	0.47032 (15)	0.24688 (11)	0.0179 (5)
C11'	0.7835 (4)	0.37808 (16)	0.20945 (14)	0.0259 (5)
H11A	0.8516	0.3863	0.1624	0.039*
H11B	0.6235	0.3537	0.2048	0.039*
H11C	0.8795	0.3341	0.2367	0.039*
C12	0.9610 (4)	0.49777 (15)	0.29108 (12)	0.0179 (5)
H12	1.0934	0.4581	0.2968	0.022*
C13	0.9533 (4)	0.58213 (15)	0.32682 (12)	0.0177 (5)
H13	1.0800	0.5993	0.3569	0.021*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0185 (3)	0.0122 (3)	0.0180 (3)	-0.00068 (18)	0.0030 (2)	-0.00096 (18)
S2	0.0217 (3)	0.0135 (3)	0.0251 (3)	-0.0034 (2)	0.0057 (2)	-0.0019 (2)
S3	0.0233 (3)	0.0177 (3)	0.0244 (3)	-0.0018 (2)	-0.0013 (2)	-0.0007 (2)
N1	0.0208 (10)	0.0120 (8)	0.0209 (10)	-0.0019 (7)	0.0041 (8)	-0.0017 (7)
N2	0.0180 (9)	0.0139 (8)	0.0192 (9)	-0.0007 (7)	0.0008 (7)	0.0009 (7)
C1	0.0205 (11)	0.0131 (10)	0.0176 (11)	0.0012 (8)	-0.0015 (9)	-0.0002 (8)
C2	0.0188 (11)	0.0159 (10)	0.0190 (11)	0.0000 (8)	-0.0014 (9)	-0.0011 (8)
C2'	0.0298 (13)	0.0226 (11)	0.0251 (13)	-0.0066 (10)	0.0095 (10)	-0.0053 (10)
C3	0.0186 (11)	0.0169 (10)	0.0168 (11)	-0.0001 (8)	-0.0023 (9)	-0.0008 (8)
C4	0.0232 (12)	0.0205 (11)	0.0272 (13)	-0.0058 (9)	-0.0092 (10)	0.0064 (9)
C5	0.0185 (12)	0.0320 (13)	0.0225 (12)	-0.0039 (10)	-0.0024 (9)	0.0099 (10)
C6	0.0182 (11)	0.0146 (10)	0.0198 (11)	0.0005 (8)	-0.0076 (9)	0.0023 (8)
C7	0.0181 (11)	0.0168 (10)	0.0204 (11)	-0.0022 (8)	0.0061 (9)	-0.0006 (8)
C8	0.0178 (11)	0.0160 (10)	0.0157 (10)	-0.0023 (8)	0.0052 (8)	0.0008 (8)
C9	0.0169 (11)	0.0199 (10)	0.0190 (11)	0.0026 (8)	0.0012 (9)	0.0026 (8)
C10	0.0165 (11)	0.0230 (11)	0.0167 (11)	-0.0019 (9)	-0.0008 (9)	0.0002 (9)
C11	0.0194 (11)	0.0179 (10)	0.0164 (11)	-0.0014 (8)	0.0038 (9)	-0.0009 (8)
C11'	0.0259 (13)	0.0222 (11)	0.0296 (13)	0.0003 (9)	0.0008 (10)	-0.0073 (10)

C12	0.0161 (11)	0.0179 (10)	0.0198 (11)	0.0026 (8)	0.0003 (9)	0.0011 (8)
C13	0.0154 (11)	0.0203 (10)	0.0175 (11)	-0.0016 (8)	-0.0008 (9)	0.0003 (8)

Geometric parameters (Å, °)

S1—C1	1.756 (2)	C6—H6	0.9500
S1—C7	1.818 (2)	C7—C8	1.511 (3)
S2—C1	1.670 (2)	C7—H7A	0.9900
S3—C4	1.703 (2)	C7—H7B	0.9900
S3—C3	1.725 (2)	C8—C13	1.391 (3)
N1—C1	1.337 (3)	C8—C9	1.396 (3)
N1—N2	1.379 (3)	C9—C10	1.385 (3)
N1—H1N	0.874 (10)	C9—H9	0.9500
N2—C2	1.283 (3)	C10—C11	1.396 (3)
C2—C3	1.462 (3)	C10—H10	0.9500
C2—C2'	1.503 (3)	C11—C12	1.393 (3)
C2'—H2'1	0.9800	C11—C11'	1.501 (3)
C2'—H2'2	0.9800	C11'—H11A	0.9800
C2'—H2'3	0.9800	C11'—H11B	0.9800
C3—C6	1.429 (3)	C11'—H11C	0.9800
C4—C5	1.354 (4)	C12—C13	1.387 (3)
C4—H4	0.9500	C12—H12	0.9500
C5—C6	1.423 (3)	C13—H13	0.9500
C5—H5	0.9500		
C1—S1—C7	101.21 (10)	C8—C7—S1	107.47 (14)
C4—S3—C3	92.08 (12)	C8—C7—H7A	110.2
C1—N1—N2	117.73 (17)	S1—C7—H7A	110.2
C1—N1—H1N	115.8 (18)	C8—C7—H7B	110.2
N2—N1—H1N	125.9 (18)	S1—C7—H7B	110.2
C2—N2—N1	118.90 (18)	H7A—C7—H7B	108.5
N1—C1—S2	122.48 (16)	C13—C8—C9	118.5 (2)
N1—C1—S1	113.31 (16)	C13—C8—C7	120.0 (2)
S2—C1—S1	124.21 (14)	C9—C8—C7	121.5 (2)
N2—C2—C3	115.14 (19)	C10—C9—C8	120.5 (2)
N2—C2—C2'	126.0 (2)	C10—C9—H9	119.7
C3—C2—C2'	118.9 (2)	C8—C9—H9	119.7
C2—C2'—H2'1	109.5	C9—C10—C11	121.1 (2)
C2—C2'—H2'2	109.5	C9—C10—H10	119.4
H2'1—C2'—H2'2	109.5	C11—C10—H10	119.4
C2—C2'—H2'3	109.5	C12—C11—C10	118.0 (2)
H2'1—C2'—H2'3	109.5	C12—C11—C11'	120.9 (2)
H2'2—C2'—H2'3	109.5	C10—C11—C11'	121.1 (2)
C6—C3—C2	128.3 (2)	C11—C11'—H11A	109.5
C6—C3—S3	111.28 (16)	C11—C11'—H11B	109.5
C2—C3—S3	120.31 (17)	H11A—C11'—H11B	109.5
C5—C4—S3	112.48 (18)	C11—C11'—H11C	109.5
C5—C4—H4	123.8	H11A—C11'—H11C	109.5

S3—C4—H4	123.8	H11B—C11'—H11C	109.5
C4—C5—C6	114.4 (2)	C13—C12—C11	120.9 (2)
C4—C5—H5	122.8	C13—C12—H12	119.5
C6—C5—H5	122.8	C11—C12—H12	119.5
C5—C6—C3	109.7 (2)	C12—C13—C8	120.9 (2)
C5—C6—H6	125.1	C12—C13—H13	119.6
C3—C6—H6	125.1	C8—C13—H13	119.6
C1—N1—N2—C2	175.2 (2)	C2—C3—C6—C5	175.4 (2)
N2—N1—C1—S2	179.03 (15)	S3—C3—C6—C5	-1.4 (2)
N2—N1—C1—S1	-1.3 (3)	C1—S1—C7—C8	-176.13 (15)
C7—S1—C1—N1	179.94 (17)	S1—C7—C8—C13	-115.3 (2)
C7—S1—C1—S2	-0.39 (17)	S1—C7—C8—C9	63.9 (2)
N1—N2—C2—C3	178.49 (18)	C13—C8—C9—C10	0.3 (3)
N1—N2—C2—C2'	-0.5 (3)	C7—C8—C9—C10	-178.9 (2)
N2—C2—C3—C6	-167.3 (2)	C8—C9—C10—C11	0.1 (3)
C2'—C2—C3—C6	11.7 (3)	C9—C10—C11—C12	-0.6 (3)
N2—C2—C3—S3	9.2 (3)	C9—C10—C11—C11'	178.8 (2)
C2'—C2—C3—S3	-171.73 (17)	C10—C11—C12—C13	0.7 (3)
C4—S3—C3—C6	0.80 (17)	C11'—C11—C12—C13	-178.7 (2)
C4—S3—C3—C2	-176.29 (18)	C11—C12—C13—C8	-0.3 (3)
C3—S3—C4—C5	0.04 (19)	C9—C8—C13—C12	-0.2 (3)
S3—C4—C5—C6	-0.9 (3)	C7—C8—C13—C12	179.1 (2)
C4—C5—C6—C3	1.5 (3)		

Hydrogen-bond geometry (Å, °)

Cg1 and Cg2 are the centroids of the S3,C3—C6 and C8—C13 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—H1N...S2 ⁱ	0.87 (2)	2.57 (2)	3.4433 (18)	176 (3)
C2'—H2'2...Cg2 ⁱⁱ	0.98	2.85	3.616 (3)	138
C12—H12...Cg1 ⁱⁱⁱ	0.95	2.89	3.560 (2)	130

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