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

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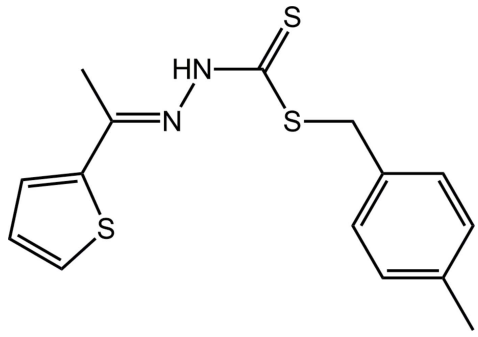
In the title compound, $C_{15}H_{16}N_2S_3$ {systematic name: [({[(4-methylphenyl)methyl]sulfanyl}methanethioyl)amino][1-(thiophen-2-yl)ethylidene]amine}, the central CN_2S_2 residue is almost planar (r.m.s. deviation = 0.0061 Å) and forms dihedral angles of 7.39 (10) and 64.91 (5)° with the thienyl 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 $\{\cdots HNCS\}_2$ synthons. The dimeric aggregates stack along the *a* axis and are are consolidated into a three-dimensional architecture *via* methyl-C—H$\cdots\pi$(benzene) and benzene-C—H$\cdots\pi$(thienyl) interactions.

Keywords: crystal structure; hydrogen bonding; dithiocarbazate; C—H$\cdots\pi$ 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

$C_{15}H_{16}N_2S_3$
M_r = 320.48
Monoclinic, $P2_1/c$
a = 5.6956 (4) Å
b = 14.3424 (9) Å
c = 18.9255 (11) Å
β = 90.263 (5)°
V = 1545.98 (17) Å^3
Z = 4
Cu $K\alpha$ 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 $I > 2\sigma(I)$
R_{int} = 0.023

2.3. Refinement

$R[F^2 > 2\sigma(F^2)]$ = 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
$\Delta\rho_{max}$ = 0.49 e Å^{-3}
$\Delta\rho_{min}$ = −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.

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N1—H1*N*$\cdots$S2^{i}	0.87 (2)	2.57 (2)	3.4433 (18)	176 (3)
C2′—H2′2$\cdots$*Cg*2^{ii}	0.98	2.85	3.616 (3)	138
C12—H12$\cdots$*Cg*1^{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: *publCIF* (Westrip, 2010).

Acknowledgements

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

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supporting information

Acta Cryst. (2015). E**71**, o475–o476 [doi:10.1107/S205698901501107X]

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

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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 $C_{15}H_{16}N_2S_3$: 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. ^{1}H-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, –SCH_2), 2.24, 2.36 (s, 6H, –CH_3), 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 (SCH_2), 15.58, 21.24 (CH_3).

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 atom was refined with N—H = 0.88±0.01 Å, and with U_{iso}(H) = 1.2U_{eq}(N).

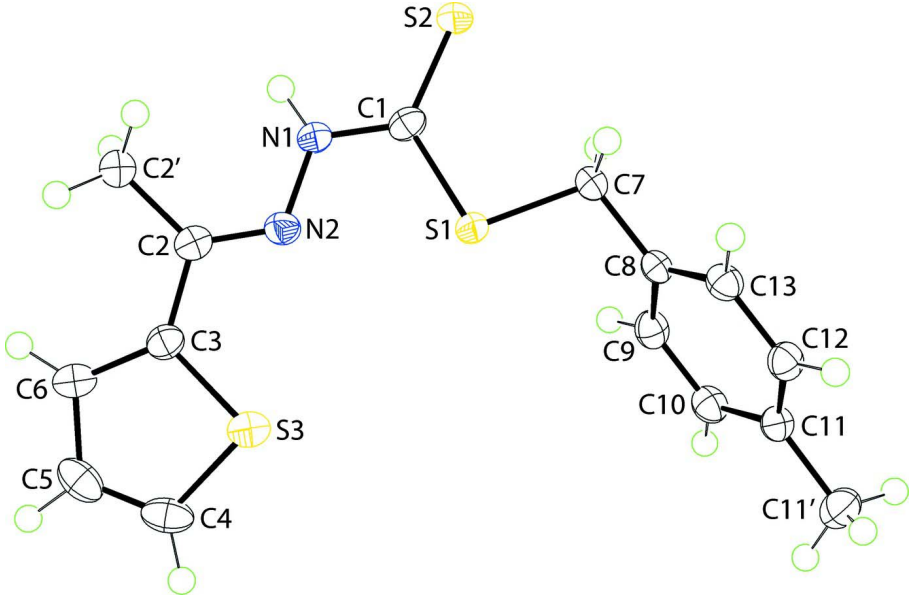

Figure 1

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

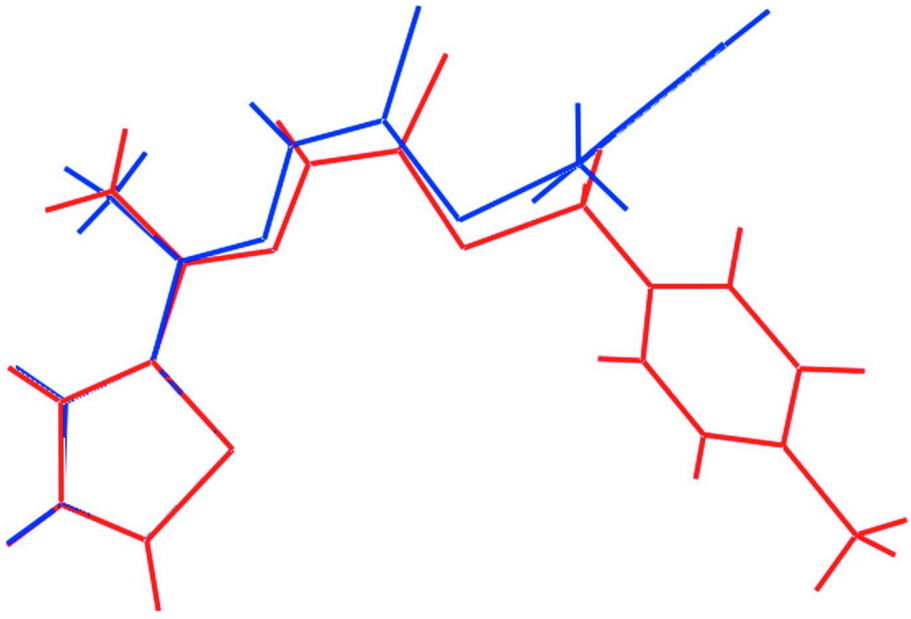

Figure 2

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.

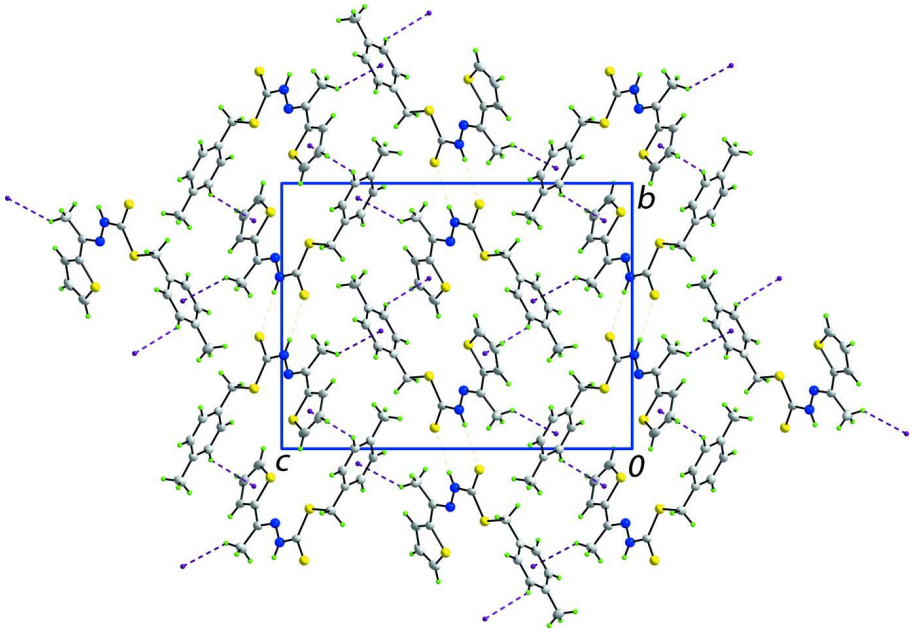

Figure 3

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

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

Crystal data

$C_{15}H_{16}N_2S_3$
M_r = 320.48
Monoclinic, $P2_1/c$
a = 5.6956 (4) Å
b = 14.3424 (9) Å
c = 18.9255 (11) Å
β = 90.263 (5)°
V = 1545.98 (17) Å^3
Z = 4
$F(000)$ = 672
D_x = 1.377 Mg m^{-3}
Cu $K\alpha$ radiation, λ = 1.54182 Å
Cell parameters from 3915 reflections
θ = 3.1–71.3°
μ = 4.30 mm^{-1}
T = 150 K
Prism, yellow
0.15 × 0.10 × 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_{int} = 0.023
θ_{max} = 71.3°, θ_{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 (Å^2)

	x	y	z	U_{iso}*/U_{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, º)

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, º)

Cg1 and Cg2 are the centroids of the S3,C3–C6 and C8–C13 rings, respectively.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*N*···S2^{i}	0.87 (2)	2.57 (2)	3.4433 (18)	176 (3)
C2′—H2′2···*Cg*2^{ii}	0.98	2.85	3.616 (3)	138
C12—H12···*Cg*1^{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.