organic compounds

N,N'-Bis[(E)-(3-methyl-2-thienyl)methylidene]ethane-1,2-diamine

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Two independent half-molecules, each being completed by inversion symmetry, comprise the asymmetric unit of the title compound, $C_{14}H_{16}N_2S_2$. The major difference between the molecules is found in the central C—C bond [the C—N—C—C torsion angles are 114.66 (18) and 128.94 (18)° in the two molecules]. The thiophene and imine groups are almost co-planar in each case [S—C—C—N torsion angles = −6.9 (2) and −3.6 (2)°]. In the crystal, the molecules aggregate into supramolecular chains *via* C—H⋯π interactions.

Related literature

For background to 2-substituted thiophenes, see: Campaigne (1984); Kleemann *et al.* (2006). For related structures, see: Wang *et al.* (2007); Wardell *et al.* (2010).
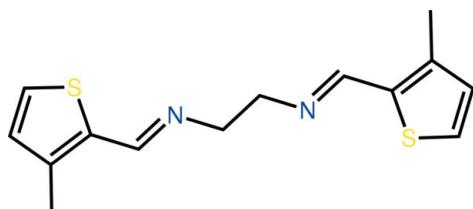
Experimental

Crystal data

$C_{14}H_{16}N_2S_2$	$\gamma = 106.066\,(1)°$
$M_r = 276.41$	$V = 675.61\,(8)$ Å^3
Triclinic, $P\bar{1}$	$Z = 2$
$a = 8.7610\,(6)$ Å	Mo $K\alpha$ radiation
$b = 8.9502\,(6)$ Å	$\mu = 0.38$ mm^{-1}
$c = 8.9853\,(6)$ Å	$T = 100$ K
$\alpha = 92.760\,(1)°$	$0.30 \times 0.30 \times 0.10$ mm
$\beta = 91.653\,(1)°$	

Data collection

Bruker SMART APEX diffractometer	6435 measured reflections
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)	3089 independent reflections
$T_{min} = 0.797$, $T_{max} = 0.862$	2822 reflections with $I > 2\sigma(I)$
	$R_{int} = 0.019$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.031$	165 parameters
$wR(F^2) = 0.100$	H-atom parameters constrained
$S = 1.10$	$\Delta\rho_{max} = 0.45$ e Å^{-3}
3089 reflections	$\Delta\rho_{min} = -0.27$ e Å^{-3}

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

$Cg1$ is the centroid of the S1,C3–C6 ring.

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
C13—H13⋯$Cg1^i$	0.95	2.89	3.6179 (19)	134

Symmetry code: (i) $-x + 1, -y + 1, -z + 1$.

Data collection: *APEX2* (Bruker, 2008); cell refinement: *SAINT* (Bruker, 2008); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *DIAMOND* (Brandenburg, 2006); software used to prepare material for publication: *publCIF* (Westrip, 2010).

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supporting information

N,*N*′-Bis[(*E*)-(3-methyl-2-thienyl)methylidene]ethane-1,2-diamine

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S1. Comment

The title bifunctional Schiff base features 2-substituted thiophene rings (Campaigne, 1984; Kleemann *et al.*, 2006) of interest owing to their putative biological activity (Wardell *et al.*, 2010). The asymmetric unit comprises two half molecules of, as each of the two independent molecules, Figs 1 and 2, is located about crystallographic centres of inversion. The major difference between the molecules is found around the central C—C bond as manifested in the C2—N1—C1—C1^{i} and C9—N2—C8—C8^{ii} torsion angles of 114.66 (18)° and 128.94 (18)°, respectively [symmetry operation *i*: 1 - *x*, 2 - *y*, -*z* and *ii*: -*x*, 2 - *y*, 2 - *z*]. Further, the twist of the thiophene ring from the imine bond is more pronounced for the first independent molecule [the N1—C2—C3—S1 torsion angle = -6.9 (2)°] compared to that found in the second independent molecule [N2—C9—C10—S2 = -3.6 (2)°]. The conformation about each of the imine N1—C2 [1.274 (2) Å] and N2—C9 [1.272 (2) Å] bonds is *E*. The observed conformations match closely that found for the unsubstituted parent compound (Wang *et al.*, 2007).

  The most prominent feature of the crystal packing is the formation of supramolecular chains comprising both independent molecules, Fig. 3, that are sustained by C—H⋯π interactions, Table 1. The chains pack in layers parallel to (1 1 0), Fig. 4.

S2. Experimental

A mixture of 3-methyl-2-thiophenecarboxaldehyde (0.43 ml, 0.004 *M*) and ethylenediamine (0.13 ml, 0.002 *M*) was stirred in dichloromethane for 3 h at room temperature. The solvent was removed under reduced pressure, and the resulting solid was dried and purified by column chromatography using a 1:3 mixture of ethyl acetate and hexane. Recrystallization was by slow evaporation of a dichloromethane solution which yielded colourless needles; yield: 81%. *M*. pt. 385–387 K.

S3. 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) set to 1.2 to 1.5U_{equiv}(C).
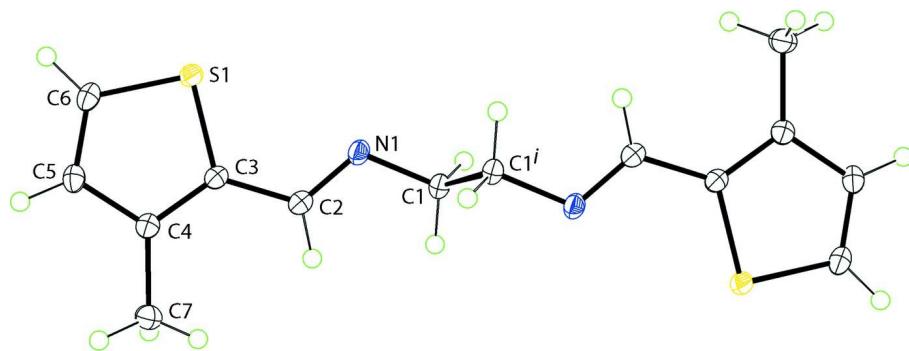
Figure 1

Molecular structure of the first independent molecule showing the atom-labelling scheme and displacement ellipsoids at the 50% probability level. Symmetry operation *i*: 1 - *x*, 2 - *y*, -*z*.
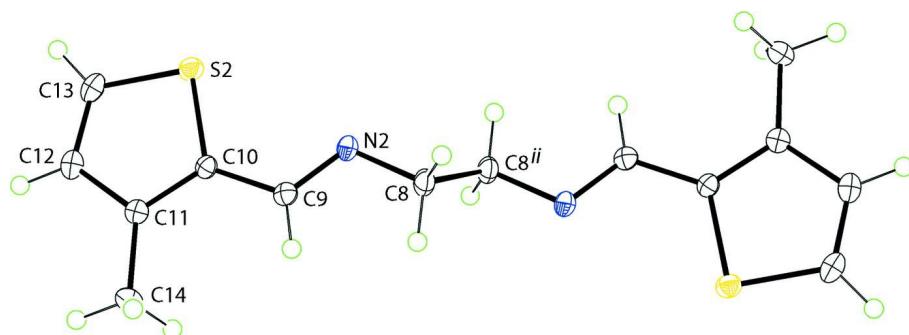
Figure 2

Molecular structure of the second independent molecule in showing the atom-labelling scheme and displacement ellipsoids at the 50% probability level. Symmetry operation *ii*: -*x*, 2 - *y*, 2 - *z*.
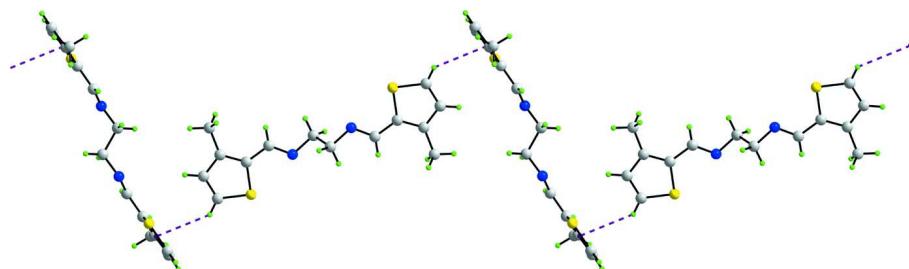
Figure 3

Supramolecular chain sustained by C—H···π contacts (shown as purple dashed lines).
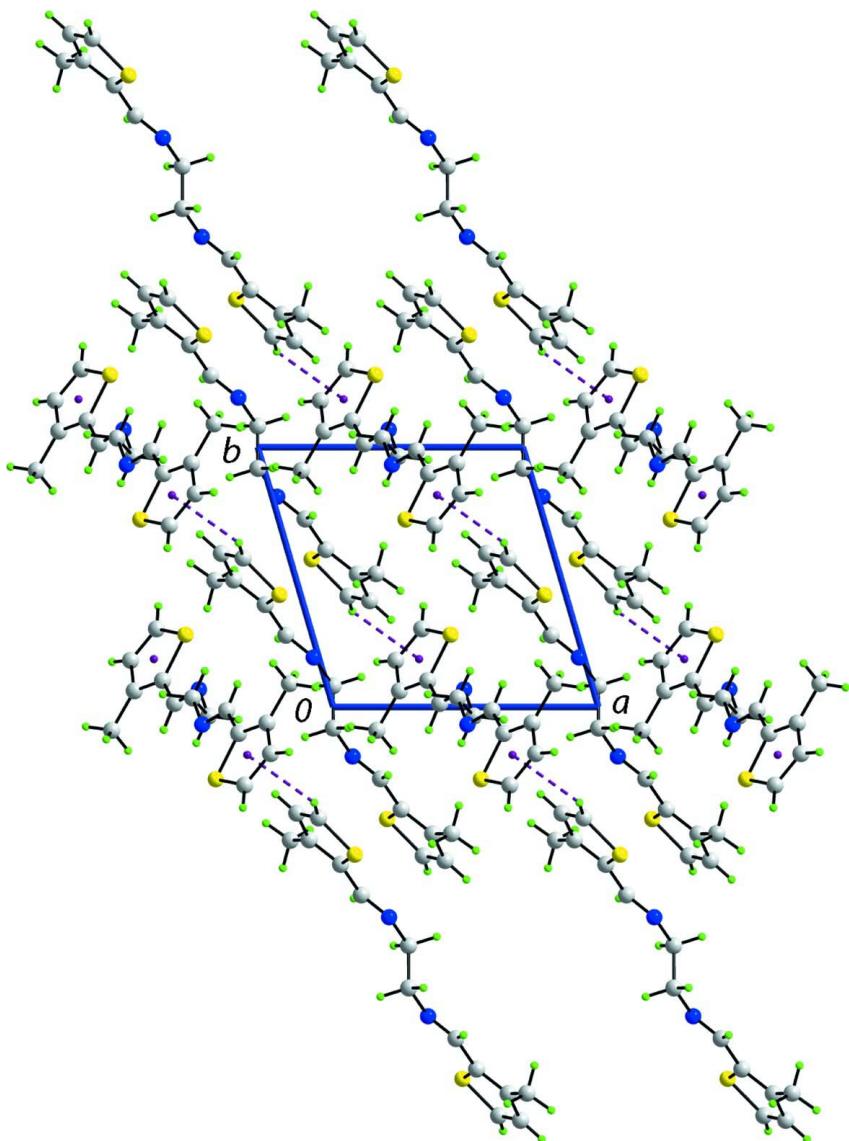
Figure 4

Unit-cell contents viewed in projection along the *c* axis. The C—H···π contacts are shown as purple dashed lines.

N,N′-**Bis[(*E*)-(3-methyl-2-thienyl)methylidene]ethane- 1,2-diamine**

Crystal data

$C_{14}H_{16}N_2S_2$	$Z = 2$
$M_r = 276.41$	$F(000) = 292$
Triclinic, $P\overline{1}$	$D_x = 1.359$ Mg m^{-3}
Hall symbol: -P 1	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 8.7610$ (6) Å	Cell parameters from 4410 reflections
$b = 8.9502$ (6) Å	$\theta = 4.3–28.3°$
$c = 8.9853$ (6) Å	$\mu = 0.38$ mm^{-1}
$\alpha = 92.760$ (1)°	$T = 100$ K
$\beta = 91.653$ (1)°	Prism, colourless
$\gamma = 106.066$ (1)°	$0.30 \times 0.30 \times 0.10$ mm
$V = 675.61$ (8) Å^3	

Data collection

Bruker SMART APEX diffractometer	6435 measured reflections
Radiation source: fine-focus sealed tube	3089 independent reflections
Graphite monochromator	2822 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.019$
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)	$\theta_{max} = 27.5°$, $\theta_{min} = 2.3°$
	$h = -11 \rightarrow 11$
	$k = -11 \rightarrow 10$
$T_{min} = 0.797$, $T_{max} = 0.862$	$l = -11 \rightarrow 11$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.031$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.100$	
$S = 1.10$	H-atom parameters constrained
3089 reflections	$w = 1/[\sigma^2(F_o^2) + (0.0508P)^2 + 0.4238P]$ where $P = (F_o^2 + 2F_c^2)/3$
165 parameters	
0 restraints	$(\Delta/\sigma)_{max} < 0.001$
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{max} = 0.45$ e Å^{-3}
	$\Delta\rho_{min} = -0.27$ e Å^{-3}

Special details

Geometry. All s.u.'s (except the s.u. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell s.u.'s are taken into account individually in the estimation of s.u.'s in distances, angles and torsion angles; correlations between s.u.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell s.u.'s is used for estimating s.u.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
S1	0.47805 (4)	0.72178 (4)	0.45069 (4)	0.01583 (12)
N1	0.48699 (16)	0.93243 (16)	0.19349 (14)	0.0171 (3)
C1	0.47949 (19)	1.03494 (19)	0.07326 (17)	0.0170 (3)
H1A	0.5554	1.1387	0.0968	0.020*
H1B	0.3712	1.0483	0.0637	0.020*
C2	0.59455 (18)	0.98652 (18)	0.29593 (17)	0.0151 (3)
H2	0.6641	1.0881	0.2890	0.018*
C3	0.61453 (18)	0.89825 (18)	0.42300 (17)	0.0147 (3)
C4	0.73245 (18)	0.93799 (18)	0.53428 (17)	0.0157 (3)
C5	0.7128 (2)	0.82044 (19)	0.63988 (17)	0.0174 (3)
H5	0.7844	0.8264	0.7228	0.021*
C6	0.5808 (2)	0.69924 (19)	0.60906 (17)	0.0180 (3)
H6	0.5493	0.6120	0.6686	0.022*
C7	0.8608 (2)	1.0898 (2)	0.5493 (2)	0.0223 (3)
H7A	0.8213	1.1682	0.6035	0.033*
H7B	0.8913	1.1247	0.4500	0.033*

H7C	0.9535	1.0756	0.6043	0.033*
S2	0.08033 (5)	0.56857 (5)	0.69562 (4)	0.01757 (12)
N2	0.01928 (16)	0.80946 (15)	0.92178 (15)	0.0166 (3)
C8	−0.0229 (2)	0.91842 (18)	1.02823 (18)	0.0179 (3)
H8A	0.0328	0.9189	1.1257	0.021*
H8B	−0.1388	0.8846	1.0427	0.021*
C9	0.09982 (18)	0.72358 (18)	0.97335 (17)	0.0151 (3)
H9	0.1320	0.7369	1.0761	0.018*
C10	0.14457 (18)	0.60595 (17)	0.88127 (17)	0.0138 (3)
C11	0.23606 (18)	0.51136 (18)	0.92386 (17)	0.0147 (3)
C12	0.25375 (19)	0.40900 (18)	0.80306 (18)	0.0177 (3)
H12	0.3134	0.3356	0.8116	0.021*
C13	0.1767 (2)	0.42700 (19)	0.67441 (19)	0.0196 (3)
H13	0.1764	0.3680	0.5836	0.023*
C14	0.30760 (19)	0.5131 (2)	1.07776 (18)	0.0191 (3)
H14A	0.3663	0.6200	1.1108	0.029*
H14B	0.3803	0.4473	1.0766	0.029*
H14C	0.2229	0.4731	1.1464	0.029*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0184 (2)	0.01340 (19)	0.0147 (2)	0.00282 (14)	0.00089 (14)	0.00138 (14)
N1	0.0216 (7)	0.0169 (6)	0.0123 (6)	0.0044 (5)	0.0017 (5)	0.0028 (5)
C1	0.0196 (7)	0.0176 (7)	0.0136 (7)	0.0046 (6)	0.0003 (6)	0.0034 (6)
C2	0.0176 (7)	0.0133 (7)	0.0152 (7)	0.0054 (6)	0.0039 (6)	0.0008 (5)
C3	0.0172 (7)	0.0130 (7)	0.0142 (7)	0.0045 (6)	0.0029 (6)	0.0009 (5)
C4	0.0185 (7)	0.0146 (7)	0.0149 (7)	0.0061 (6)	0.0014 (6)	0.0001 (6)
C5	0.0229 (8)	0.0178 (7)	0.0133 (7)	0.0090 (6)	−0.0003 (6)	0.0006 (6)
C6	0.0250 (8)	0.0171 (7)	0.0140 (7)	0.0087 (6)	0.0034 (6)	0.0031 (6)
C7	0.0213 (8)	0.0178 (8)	0.0256 (8)	0.0024 (6)	−0.0047 (6)	0.0022 (6)
S2	0.0210 (2)	0.0169 (2)	0.0142 (2)	0.00442 (15)	−0.00034 (14)	0.00084 (14)
N2	0.0193 (6)	0.0113 (6)	0.0188 (6)	0.0040 (5)	−0.0001 (5)	−0.0004 (5)
C8	0.0230 (8)	0.0132 (8)	0.0187 (7)	0.0068 (6)	0.0021 (6)	0.0007 (6)
C9	0.0148 (7)	0.0129 (7)	0.0159 (7)	0.0010 (5)	0.0007 (5)	0.0015 (6)
C10	0.0148 (7)	0.0115 (7)	0.0144 (7)	0.0022 (5)	0.0018 (5)	0.0012 (5)
C11	0.0134 (7)	0.0138 (7)	0.0160 (7)	0.0017 (5)	0.0032 (5)	0.0024 (6)
C12	0.0163 (7)	0.0141 (7)	0.0225 (8)	0.0034 (6)	0.0059 (6)	0.0011 (6)
C13	0.0214 (8)	0.0158 (7)	0.0199 (8)	0.0026 (6)	0.0061 (6)	−0.0026 (6)
C14	0.0171 (7)	0.0228 (8)	0.0186 (8)	0.0069 (6)	−0.0005 (6)	0.0034 (6)

Geometric parameters (Å, º)

S1—C6	1.7119 (16)	S2—C13	1.7125 (17)
S1—C3	1.7309 (16)	S2—C10	1.7318 (16)
N1—C2	1.274 (2)	N2—C9	1.272 (2)
N1—C1	1.4621 (19)	N2—C8	1.460 (2)
C1—C1ⁱ	1.525 (3)	C8—C8ⁱⁱ	1.520 (3)

C1—H1A	0.9900	C8—H8A	0.9900
C1—H1B	0.9900	C8—H8B	0.9900
C2—C3	1.453 (2)	C9—C10	1.453 (2)
C2—H2	0.9500	C9—H9	0.9500
C3—C4	1.377 (2)	C10—C11	1.377 (2)
C4—C5	1.429 (2)	C11—C12	1.426 (2)
C4—C7	1.502 (2)	C11—C14	1.499 (2)
C5—C6	1.360 (2)	C12—C13	1.361 (2)
C5—H5	0.9500	C12—H12	0.9500
C6—H6	0.9500	C13—H13	0.9500
C7—H7A	0.9800	C14—H14A	0.9800
C7—H7B	0.9800	C14—H14B	0.9800
C7—H7C	0.9800	C14—H14C	0.9800
C6—S1—C3	91.47 (8)	C13—S2—C10	91.55 (8)
C2—N1—C1	116.35 (13)	C9—N2—C8	116.78 (14)
N1—C1—C1[i]	109.83 (16)	N2—C8—C8[ii]	110.34 (17)
N1—C1—H1A	109.7	N2—C8—H8A	109.6
C1[i]—C1—H1A	109.7	C8[ii]—C8—H8A	109.6
N1—C1—H1B	109.7	N2—C8—H8B	109.6
C1[i]—C1—H1B	109.7	C8[ii]—C8—H8B	109.6
H1A—C1—H1B	108.2	H8A—C8—H8B	108.1
N1—C2—C3	122.28 (14)	N2—C9—C10	122.61 (14)
N1—C2—H2	118.9	N2—C9—H9	118.7
C3—C2—H2	118.9	C10—C9—H9	118.7
C4—C3—C2	127.93 (14)	C11—C10—C9	127.42 (14)
C4—C3—S1	111.67 (12)	C11—C10—S2	111.68 (12)
C2—C3—S1	120.39 (12)	C9—C10—S2	120.89 (11)
C3—C4—C5	111.63 (14)	C10—C11—C12	111.52 (14)
C3—C4—C7	124.67 (14)	C10—C11—C14	124.84 (14)
C5—C4—C7	123.60 (14)	C12—C11—C14	123.64 (14)
C6—C5—C4	112.87 (14)	C13—C12—C11	113.24 (14)
C6—C5—H5	123.6	C13—C12—H12	123.4
C4—C5—H5	123.6	C11—C12—H12	123.4
C5—C6—S1	112.33 (12)	C12—C13—S2	112.00 (12)
C5—C6—H6	123.8	C12—C13—H13	124.0
S1—C6—H6	123.8	S2—C13—H13	124.0
C4—C7—H7A	109.5	C11—C14—H14A	109.5
C4—C7—H7B	109.5	C11—C14—H14B	109.5
H7A—C7—H7B	109.5	H14A—C14—H14B	109.5
C4—C7—H7C	109.5	C11—C14—H14C	109.5
H7A—C7—H7C	109.5	H14A—C14—H14C	109.5
H7B—C7—H7C	109.5	H14B—C14—H14C	109.5
C2—N1—C1—C1[i]	114.66 (18)	C9—N2—C8—C8[ii]	128.94 (18)
C1—N1—C2—C3	179.26 (14)	C8—N2—C9—C10	177.52 (14)
N1—C2—C3—C4	174.57 (16)	N2—C9—C10—C11	177.29 (16)
N1—C2—C3—S1	−6.9 (2)	N2—C9—C10—S2	−3.6 (2)

C6—S1—C3—C4	−1.13 (13)	C13—S2—C10—C11	−0.31 (12)
C6—S1—C3—C2	−179.90 (13)	C13—S2—C10—C9	−179.53 (13)
C2—C3—C4—C5	−179.55 (15)	C9—C10—C11—C12	179.52 (15)
S1—C3—C4—C5	1.80 (17)	S2—C10—C11—C12	0.36 (17)
C2—C3—C4—C7	3.9 (3)	C9—C10—C11—C14	0.1 (3)
S1—C3—C4—C7	−174.74 (13)	S2—C10—C11—C14	−179.05 (12)
C3—C4—C5—C6	−1.7 (2)	C10—C11—C12—C13	−0.2 (2)
C7—C4—C5—C6	174.86 (15)	C14—C11—C12—C13	179.18 (14)
C4—C5—C6—S1	0.86 (18)	C11—C12—C13—S2	0.01 (18)
C3—S1—C6—C5	0.14 (13)	C10—S2—C13—C12	0.17 (13)

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

Hydrogen-bond geometry (Å, º)

Cg1 is the centroid of the S1,C3–C6 ring.

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
C13—H13⋯Cg1[iii]	0.95	2.89	3.6179 (19)	134

Symmetry code: (iii) −x+1, −y+1, −z+1.