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Crystal structure of (2-chloroethyl)[2-(methylsulfanyl)benzyl]ammonium chloride

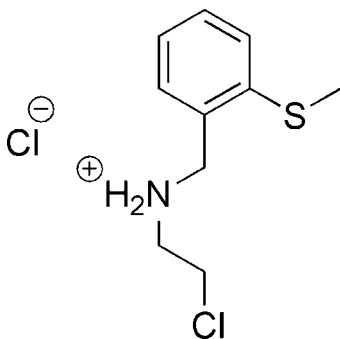
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In the title molecular salt, $C_{10}H_{15}ClNS^+ \cdot Cl^-$, the cation is $[R'R''NH_2]^+$, where R' is 2-MeS-C₆H₄CH₂- and R'' is -CH₂CH₂Cl, and the anion is Cl⁻. In the cation, the N atom is protonated with sp^3 -hybridization and with a tetrahedral geometry. In the crystal, the anions are connected to the cations through two pairs of N—H...Cl hydrogen bonds, generating a four-centred inversion dimer with an $R_4^2(8)$ ring motif.

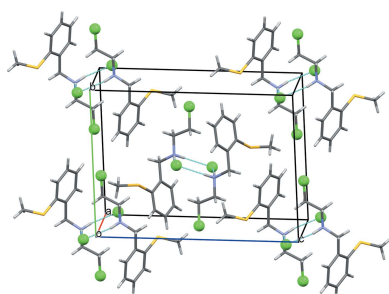
1. Chemical context

Chloroethyl-functionalized derivatives containing S- and N-donor sites are used for the preparation of (S, N, S/Se/Te/P/As/Sb)-type tridentate hybrid ligands by nucleophilic substitution of the chloro (Cl⁻) group by RS⁻, ArSe⁻, ArTe⁻, Ph₂P⁻, Ar₂As⁻ (Kumar *et al.*, 2008a; Singh *et al.*, 1999; Singh & Singh, 2010, 2012; Kumar *et al.*, 2008b). Metal complexes of this type of hybrid ligand are important and have found applications as catalysts in organic synthesis (Singh *et al.*, 2013). Keeping this in mind, it was thought worthwhile to synthesise and characterise the title molecular salt. We report herein on its synthesis, by chlorination of 2-(2-methylthio)benzylamino)-ethanol using thionyl chloride, and on its crystal structure.



2. Structural commentary

In the cation of the title molecular salt (Fig. 1), the -CH₂-N⁺H₂-CH₂-CH₂-Cl substituent has an extended conformation with all of the non-H atoms lying in a plane [maximum deviation = 0.032 (4) Å for atom C8]. The N1 atom is protonated with sp^3 -hybridization and has a tetrahedral geometry. The S1 atom lies in the plane of the benzene ring to which it is attached while the methyl C10 atom is displaced from the plane of the benzene ring by 1.773 (5) Å.



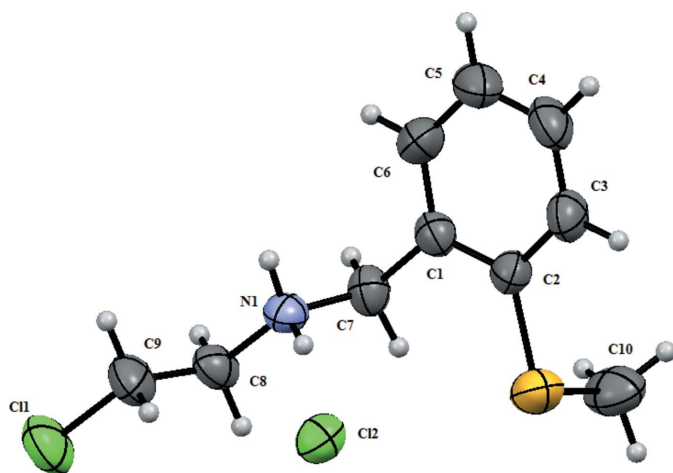


Figure 1
The molecular structure of the title molecular salt, showing the atom labelling. The displacement ellipsoids are drawn at the 50% probability level.

The title molecular salt was also characterised by NMR and FT-IR spectroscopy. In the proton NMR spectrum, the signals for the NCH_2 and CH_2Cl protons gave two triplets at 3.25 and 3.9 p.p.m., respectively. The $[\text{C}_{10}\text{H}_{15}\text{ClSN}]^+$ cation is a secondary ammonium ion in which the N atom is protonated and hence undergoes sp^3 hybridization, resulting in a tetrahedral geometry around the N atom. This was confirmed by NMR as the >NH_2^+ protons are highly deshielded and are observed as a broad singlet at 10.03 p.p.m. In the FT-IR spectrum of title salt, the N-H stretching band was observed at 1569 cm^{-1} .

3. Supramolecular features

In the crystal, the cation and anion are connected through two pairs of $\text{N-H}\cdots\text{Cl}$ hydrogen bonds. These hydrogen bonds

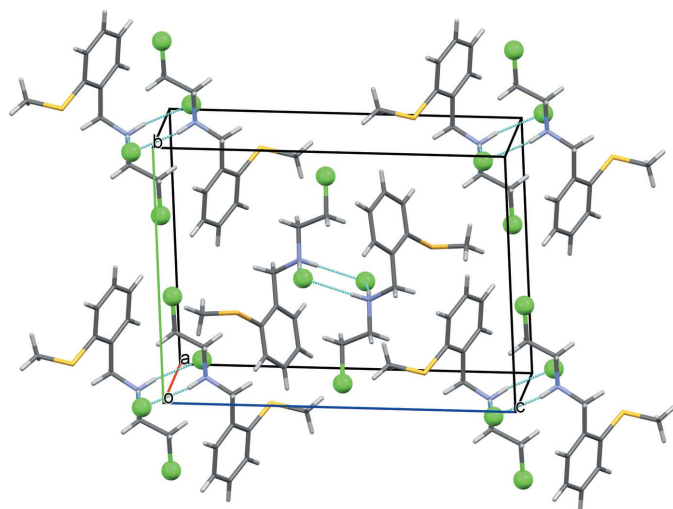


Figure 2
The crystal packing of the title molecular salt, viewed along the a axis. The $\text{N-H}\cdots\text{Cl}$ hydrogen bonds are shown as dashed lines (see Table 1 for details).

Table 1
Hydrogen-bond geometry (\AA , $^\circ$).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{N1-H1B}\cdots\text{Cl2}$	0.89	2.21	3.090 (3)	169
$\text{N1-H1A}\cdots\text{Cl2}^i$	0.89	2.32	3.163 (3)	158

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

result in the formation of four-centred inversion dimers with an $R_2^2(8)$ ring motif (Table 1 and Fig. 2).

4. Database survey

A search of the Cambridge Structural Database (Version 5.36; Groom & Allen, 2014) found no hits for similar compounds. However, tridentate (S, N, S/Se/Te)-type ligands containing the cationic part of the title salt and their Pd^{II} and Ru^{II} complexes have been synthesised and structurally characterized (Kumar *et al.*, 2008a; Singh & Singh, 2012; Singh *et al.*, 2012).

5. Synthesis and crystallization

The synthesis of the title compound is illustrated in Fig. 3. 2-(2-Methylthio)benzylamino)ethanol (2 g, 10 mmol) was dissolved in 20 ml of dry chloroform and the solution was cooled in an ice bath. Freshly distilled SOCl_2 (3 ml, 40 mmol) dissolved in 20 ml of dry chloroform was added to it dropwise over a period of 15 min. When the addition was complete, the temperature of the reaction mixture was increased slowly and the mixture was stirred under reflux for 6 h. Thereafter, the reaction mixture was cooled and concentrated to 10 ml on a rotary evaporator, giving a light-brown solid. The solid was dissolved in 10 ml of methanol, boiled with a pinch of activated charcoal and filtered. The filtrate was treated with 20 ml of diethyl ether. It gave a white crystalline product (caution: eye and skin irritant), which was filtered, washed with diethyl ether ($10\text{ ml} \times 4$) and dried between the folds of filter paper. Colourless prisms of the title compound were grown in ethanol by slow evaporation of the solvent (yield: 70%; m.p.: 413 K; $\Lambda_M = 3.0\text{ cm}^2\text{ mol}^{-1}\text{ ohm}^{-1}$. Elemental analysis, found (calc.): C, 47.87 (47.68), H, 5.95 (5.99), N, 5.68 (5.55) %; ^1H NMR (CDCl_3 , 298 K): δ (vs TMS): 2.55 (*s*, 3H, SCH_3), 3.25 (*t*, $J = 6.09\text{ Hz}$, 2H, H_1), 3.9 (*t*, $J = 6.6\text{ Hz}$, 2H, H_2), 4.94 (*s*, 2H, H_3), 7.26 (*t*, $J = 6.96\text{ Hz}$, 1H, H_8), 7.34–7.46 (*m*, 2H, $\text{H}_{6,7}$), 7.72–7.74 (*d*, $J = 7.5\text{ Hz}$, 1H, H_9), 10.03 (*bs*, 2H, NH_2^+). $^{13}\text{C}\{^1\text{H}\}$ NMR

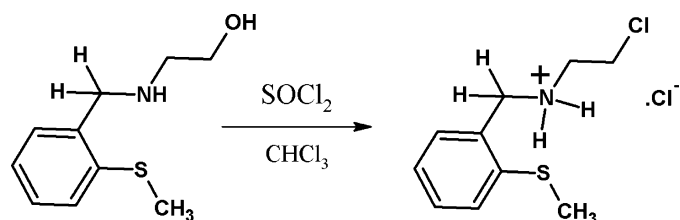


Figure 3
The synthesis of the title molecular salt.

(CDCl₃, 298 K): δ (vs TMS): 16.85 (SCH₃), 48.17 (C₂), 49.27 (C₁), 57.12 (C₃), 126.26 (C₆), 127.89 (C₇), 128.87 (C₄), 130.25 (C₈), 131.50 (C₉), 138.95 (C₅). FT-IR (KBr, cm⁻¹): 3415 (s), 1569 (b) (N-H), 1590 (C-N), 763 (C-S).

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The hydrogen atoms attached to atom N1 were located in a difference Fourier map. In the final cycles of refinement they were included in calculated positions, as were the C-bound H atoms, and treated as riding atoms: N-H = 0.89 Å, C-H = 0.93–0.97 Å with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ for methyl H atoms and = $1.2U_{\text{eq}}(\text{N,C})$ for other H atoms.

Acknowledgements

PRK thanks Professor Ajai K. Singh of IIT Delhi, India, for his valuable guidance during his PhD studies. BSP thanks Dr H. C. Devarajegowda, Department of Physics, Yuvarajas College (constituent), University of Mysore, for his support.

References

- Bruker (2013). *APEX2*, *SAINT* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Groom, C. R. & Allen, F. H. (2014). *Angew. Chem. Int. Ed.* **53**, 662–671.
- Kumar, P. R., Upreti, S. & Singh, A. K. (2008a). *Inorg. Chim. Acta*, **361**, 1426–1436.
- Kumar, P. R., Upreti, S. & Singh, A. K. (2008b). *Polyhedron*, **27**, 1610–1622.
- Macrae, C. F., Bruno, I. J., Chisholm, J. A., Edgington, P. R., McCabe, P., Pidcock, E., Rodriguez-Monge, L., Taylor, R., van de Streek, J. & Wood, P. A. (2008). *J. Appl. Cryst.* **41**, 466–470.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Sheldrick, G. M. (2015). *Acta Cryst.* **C71**, 3–8.
- Singh, A. K., Amburose, C. V., Kraemer, T. S. & Jasinski, J. P. (1999). *J. Organomet. Chem.* **592**, 251–257.

Table 2

Experimental details.

Crystal data	
Chemical formula	C ₁₀ H ₁₅ CINS ⁺ ·Cl ⁻
M_r	252.19
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	298
a, b, c (Å)	6.5717 (10), 11.8058 (17), 16.201 (2)
β (°)	97.374 (3)
V (Å ³)	1246.5 (3)
Z	4
Radiation type	Mo $K\alpha$
μ (mm ⁻¹)	0.65
Crystal size (mm)	0.28 × 0.24 × 0.20
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan (<i>SADABS</i> ; Bruker, 2013)
$T_{\text{min}}, T_{\text{max}}$	0.839, 0.881
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	9002, 2255, 1584
R_{int}	0.100
$(\sin \theta/\lambda)_{\text{max}}$ (Å ⁻¹)	0.600
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.065, 0.158, 1.04
No. of reflections	2255
No. of parameters	128
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å ⁻³)	0.50, -0.23

Computer programs: *APEX2* and *SAINT* (Bruker, 2013), *SHELXS97* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2015), *Mercury* (Macrae *et al.*, 2008) and *PLATON* (Spek, 2009).

- Singh, P., Das, D., Kumar, A. & Singh, A. K. (2012). *Inorg. Chem. Commun.* **15**, 163–166.
- Singh, P., Das, D., Prakash, O. & Singh, A. K. (2013). *Inorg. Chim. Acta*, **394**, 77–84.
- Singh, P. & Singh, A. K. (2010). *Eur. J. Inorg. Chem.* pp. 4187–4195.
- Singh, P. & Singh, A. K. (2012). *Inorg. Chim. Acta*, **387**, 441–445.
- Spek, A. L. (2009). *Acta Cryst.* **D65**, 148–155.

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Acta Cryst. (2015). E71, 621-623 [doi:10.1107/S2056989015008221]

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Computing details

Data collection: *APEX2* (Bruker, 2013); cell refinement: *SAINTE* (Bruker, 2013); data reduction: *SAINTE* (Bruker, 2013); program(s) used to solve structure: *SHELXS97* (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) and *PLATON* (Spek, 2009).

(2-Chloroethyl)[2-(methylsulfanyl)benzyl]ammonium chloride

Crystal data

$C_{10}H_{15}ClNS^+ \cdot Cl^-$
 $M_r = 252.19$
 Monoclinic, $P2_1/n$
 $a = 6.5717$ (10) Å
 $b = 11.8058$ (17) Å
 $c = 16.201$ (2) Å
 $\beta = 97.374$ (3)°
 $V = 1246.5$ (3) Å³
 $Z = 4$

$F(000) = 528$
 $D_x = 1.344$ Mg m⁻³
 Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
 $\theta = 2.1$ – 25.0 °
 $\mu = 0.65$ mm⁻¹
 $T = 298$ K
 Prism, colourless
 $0.28 \times 0.24 \times 0.20$ mm

Data collection

Bruker APEXII CCD
 diffractometer
 Radiation source: fine-focus sealed tube
 phi and ω scans
 Absorption correction: multi-scan
 (*SADABS*; Bruker, 2013)
 $T_{\min} = 0.839$, $T_{\max} = 0.881$
 9002 measured reflections

2255 independent reflections
 1584 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.100$
 $\theta_{\max} = 25.3$ °, $\theta_{\min} = 2.1$ °
 $h = -7 \rightarrow 7$
 $k = -14 \rightarrow 14$
 $l = -19 \rightarrow 19$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.065$
 $wR(F^2) = 0.158$
 $S = 1.04$
 2255 reflections
 128 parameters
 0 restraints

Hydrogen site location: inferred from
 neighbouring sites
 H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0727P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.50$ e Å⁻³
 $\Delta\rho_{\min} = -0.23$ 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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
S1	0.73384 (17)	-0.10230 (10)	0.26820 (8)	0.0632 (4)
Cl1	0.2925 (2)	0.37387 (9)	0.02280 (9)	0.0769 (4)
N1	0.3518 (5)	0.0518 (2)	0.10476 (19)	0.0437 (8)
H1A	0.2751	0.0208	0.0613	0.052*
H1B	0.4827	0.0411	0.0980	0.052*
C1	0.3504 (6)	-0.1317 (3)	0.1757 (2)	0.0442 (9)
C2	0.5336 (6)	-0.1815 (3)	0.2109 (2)	0.0443 (9)
C4	0.4120 (7)	-0.3622 (4)	0.1571 (3)	0.0615 (12)
H4	0.4340	-0.4393	0.1503	0.074*
C3	0.5612 (7)	-0.2969 (3)	0.2011 (3)	0.0557 (11)
H3	0.6828	-0.3307	0.2247	0.067*
C5	0.2319 (8)	-0.3142 (4)	0.1233 (3)	0.0675 (13)
H5	0.1301	-0.3584	0.0940	0.081*
C6	0.2013 (7)	-0.1992 (4)	0.1330 (3)	0.0612 (12)
H6	0.0777	-0.1669	0.1102	0.073*
C8	0.3102 (6)	0.1754 (3)	0.1051 (3)	0.0497 (10)
H8A	0.4013	0.2113	0.1493	0.060*
H8B	0.1701	0.1884	0.1157	0.060*
C7	0.3103 (6)	-0.0073 (3)	0.1812 (2)	0.0489 (10)
H7A	0.1683	0.0047	0.1896	0.059*
H7B	0.3968	0.0241	0.2287	0.059*
C9	0.3421 (8)	0.2266 (3)	0.0230 (3)	0.0657 (13)
H9A	0.2511	0.1906	-0.0212	0.079*
H9B	0.4822	0.2136	0.0125	0.079*
C10	0.6669 (8)	-0.1210 (4)	0.3711 (3)	0.0762 (15)
H10A	0.5336	-0.0892	0.3741	0.114*
H10B	0.7662	-0.0834	0.4104	0.114*
H10C	0.6651	-0.2003	0.3840	0.114*
Cl2	0.80532 (15)	0.04958 (9)	0.07270 (6)	0.0537 (3)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0557 (7)	0.0679 (8)	0.0632 (8)	-0.0149 (6)	-0.0034 (6)	0.0005 (6)
Cl1	0.0879 (9)	0.0413 (7)	0.1012 (10)	0.0074 (6)	0.0111 (7)	0.0136 (6)
N1	0.0465 (19)	0.0362 (18)	0.0467 (19)	0.0002 (14)	-0.0010 (15)	-0.0050 (15)
C1	0.053 (2)	0.038 (2)	0.042 (2)	0.0005 (19)	0.0068 (19)	0.0023 (17)
C2	0.050 (2)	0.041 (2)	0.040 (2)	0.0010 (18)	-0.0013 (18)	0.0014 (18)
C4	0.088 (4)	0.035 (2)	0.060 (3)	0.005 (2)	0.005 (3)	0.005 (2)

C3	0.064 (3)	0.042 (2)	0.058 (3)	0.011 (2)	-0.003 (2)	0.004 (2)
C5	0.088 (4)	0.050 (3)	0.058 (3)	-0.018 (3)	-0.011 (3)	0.001 (2)
C6	0.054 (3)	0.058 (3)	0.066 (3)	-0.005 (2)	-0.013 (2)	0.005 (2)
C8	0.049 (2)	0.032 (2)	0.067 (3)	0.0023 (18)	0.006 (2)	-0.001 (2)
C7	0.056 (2)	0.043 (2)	0.048 (2)	0.0082 (19)	0.007 (2)	0.0038 (18)
C9	0.085 (3)	0.037 (2)	0.071 (3)	0.002 (2)	-0.003 (3)	0.004 (2)
C10	0.084 (4)	0.084 (4)	0.058 (3)	-0.020 (3)	-0.001 (3)	-0.014 (3)
Cl2	0.0499 (6)	0.0577 (7)	0.0524 (6)	0.0044 (5)	0.0020 (5)	-0.0074 (5)

Geometric parameters (Å, °)

S1—C2	1.776 (4)	C3—H3	0.9300
S1—C10	1.792 (5)	C5—C6	1.384 (6)
Cl1—C9	1.768 (4)	C5—H5	0.9300
N1—C7	1.477 (5)	C6—H6	0.9300
N1—C8	1.485 (5)	C8—C9	1.501 (6)
N1—H1A	0.8900	C8—H8A	0.9700
N1—H1B	0.8900	C8—H8B	0.9700
C1—C6	1.378 (5)	C7—H7A	0.9700
C1—C2	1.394 (5)	C7—H7B	0.9700
C1—C7	1.496 (5)	C9—H9A	0.9700
C2—C3	1.386 (5)	C9—H9B	0.9700
C4—C5	1.362 (6)	C10—H10A	0.9600
C4—C3	1.373 (6)	C10—H10B	0.9600
C4—H4	0.9300	C10—H10C	0.9600
C2—S1—C10	99.7 (2)	N1—C8—C9	110.2 (3)
C7—N1—C8	114.0 (3)	N1—C8—H8A	109.6
C7—N1—H1A	108.8	C9—C8—H8A	109.6
C8—N1—H1A	108.8	N1—C8—H8B	109.6
C7—N1—H1B	108.8	C9—C8—H8B	109.6
C8—N1—H1B	108.8	H8A—C8—H8B	108.1
H1A—N1—H1B	107.6	N1—C7—C1	111.1 (3)
C6—C1—C2	118.8 (4)	N1—C7—H7A	109.4
C6—C1—C7	118.6 (4)	C1—C7—H7A	109.4
C2—C1—C7	122.6 (3)	N1—C7—H7B	109.4
C3—C2—C1	119.1 (4)	C1—C7—H7B	109.4
C3—C2—S1	118.6 (3)	H7A—C7—H7B	108.0
C1—C2—S1	122.3 (3)	C8—C9—Cl1	110.5 (3)
C5—C4—C3	120.1 (4)	C8—C9—H9A	109.5
C5—C4—H4	120.0	Cl1—C9—H9A	109.5
C3—C4—H4	120.0	C8—C9—H9B	109.5
C4—C3—C2	121.1 (4)	Cl1—C9—H9B	109.5
C4—C3—H3	119.5	H9A—C9—H9B	108.1
C2—C3—H3	119.5	S1—C10—H10A	109.5
C4—C5—C6	119.6 (4)	S1—C10—H10B	109.5
C4—C5—H5	120.2	H10A—C10—H10B	109.5
C6—C5—H5	120.2	S1—C10—H10C	109.5

C1—C6—C5	121.3 (4)	H10A—C10—H10C	109.5
C1—C6—H6	119.3	H10B—C10—H10C	109.5
C5—C6—H6	119.3		
C6—C1—C2—C3	0.7 (6)	C3—C4—C5—C6	0.6 (7)
C7—C1—C2—C3	-178.2 (4)	C2—C1—C6—C5	-1.2 (6)
C6—C1—C2—S1	-179.2 (3)	C7—C1—C6—C5	177.8 (4)
C7—C1—C2—S1	1.9 (5)	C4—C5—C6—C1	0.5 (7)
C10—S1—C2—C3	-87.1 (4)	C7—N1—C8—C9	-175.9 (3)
C10—S1—C2—C1	92.8 (4)	C8—N1—C7—C1	178.6 (3)
C5—C4—C3—C2	-1.1 (7)	C6—C1—C7—N1	-81.3 (5)
C1—C2—C3—C4	0.4 (6)	C2—C1—C7—N1	97.7 (4)
S1—C2—C3—C4	-179.7 (3)	N1—C8—C9—C11	179.9 (3)

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>
N1—H1B \cdots C12	0.89	2.21	3.090 (3)	169
N1—H1A \cdots C12 ⁱ	0.89	2.32	3.163 (3)	158

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