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4-Chloro-2-methyl-N-(2-methylphenyl)-benzenesulfonamide

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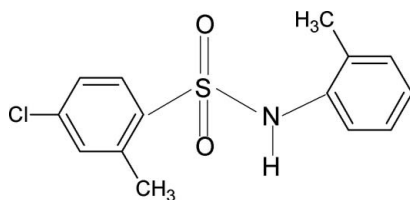
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Key indicators: single-crystal X-ray study; $T = 299$ K; mean $\sigma(\text{C}-\text{C}) = 0.005$ Å; R factor = 0.072; wR factor = 0.235; data-to-parameter ratio = 13.3.

In the crystal structure of the title compound, $\text{C}_{14}\text{H}_{14}\text{ClNO}_2\text{S}$, the two aromatic rings are tilted relative to each other by $45.8(1)^\circ$. In the crystal, inversion dimers linked by pairs of $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds occur.

Related literature

For related structures, see: Gelbrich *et al.* (2007); Gowda *et al.* (2009a,b); Perlovich *et al.* (2006).



Experimental

Crystal data

$\text{C}_{14}\text{H}_{14}\text{ClNO}_2\text{S}$
 $M_r = 295.77$
 Triclinic, $P\bar{1}$
 $a = 8.1200(8)$ Å

$b = 8.1832(8)$ Å
 $c = 10.985(1)$ Å
 $\alpha = 95.81(1)^\circ$
 $\beta = 96.92(1)^\circ$

$\gamma = 106.82(1)^\circ$
 $V = 686.46(11)$ Å³
 $Z = 2$
 Cu $K\alpha$ radiation

$\mu = 3.86$ mm⁻¹
 $T = 299$ K
 $0.50 \times 0.48 \times 0.18$ mm

Data collection

Enraf–Nonius CAD-4 diffractometer
 Absorption correction: ψ scan (North *et al.*, 1968)
 $T_{\min} = 0.228$, $T_{\max} = 0.500$
 2572 measured reflections

2366 independent reflections
 2194 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.054$
 3 standard reflections
 frequency: 120 min
 intensity decay: 2.5%

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.072$
 $wR(F^2) = 0.235$
 $S = 1.10$
 2366 reflections
 178 parameters

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\text{max}} = 0.82$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.63$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{N1}-\text{H1N}\cdots\text{O2}^i$	0.87 (4)	2.14 (4)	2.993 (4)	167 (3)

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

Data collection: *CAD-4-PC* (Enraf–Nonius, 1996); cell refinement: *CAD-4-PC*; data reduction: *REDU4* (Stoe & Cie, 1987); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *PLATON* (Spek, 2009); software used to prepare material for publication: *SHELXL97*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BT2900).

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supporting information

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4-Chloro-2-methyl-*N*-(2-methylphenyl)benzenesulfonamide

B. Thimme Gowda, Sabine Foro, P. G. Nirmala, Hiromitsu Terao and Hartmut Fuess

S1. Comment

In the present work, as part of a study of substituent effects on the structures of *N*-(aryl)-arylsulfonamides, the structure of 4-chloro-2-methyl-*N*-(2-methylphenyl)benzenesulfonamide has been determined (Gowda *et al.* 2009*a,b*). The conformations of the N—C bonds in the C—SO₂—NH—C segment have *trans* and *gauche* torsion angles with the S=O bonds (Fig. 1). The molecule is bent at the S atom with the C—SO₂—NH—C torsion angle of 73.0 (2). The *ortho*-methyl group in the sulfonyl benzene ring is oriented away from the S=O bonds and so also the *ortho*-methyl group in the anilino benzene ring from the N—H bond. The two benzene rings are tilted relative to each other by 45.8 (1)°, compared with the values of 86.6 (2)° (molecule 1) and 83.0 (2)° (molecule 2), in the two independent molecules of 4-chloro-2-methyl-*N*-(phenyl)benzenesulfonamide (Gowda *et al.*, 2009*a*). The other bond parameters in the title compound are similar to those observed in 2,4-dimethyl-*N*-(phenyl)benzenesulfonamide (Gowda *et al.*, 2009*b*) and other aryl sulfonamides (Perlovich *et al.*, 2006; Gelbrich *et al.*, 2007). The crystal packing of the molecules is characterized by N—H⋯O(S) hydrogen bonds (Table 1, Fig.2).

S2. Experimental

A solution of *m*-chlorotoluene (10 cc) in chloroform (40 cc) was treated dropwise with chlorosulfonic acid (25 cc) at 0 °C. After the initial evolution of hydrogen chloride subsided, the reaction mixture was brought to room temperature and poured into crushed ice in a beaker. The chloroform layer was separated, washed with cold water and allowed to evaporate slowly. The residual 4-chloro-2-methylbenzenesulfonylchloride was treated with *o*-toluidine in the stoichiometric ratio and boiled for ten minutes. The reaction mixture was then cooled to room temperature and added to ice cold water (100 cc). The resultant solid 4-chloro-2-methyl-*N*-(2-methylphenyl)benzenesulfonamide was filtered under suction and washed thoroughly with cold water. It was then recrystallized to constant melting point from dilute ethanol. The purity of the compound was checked and characterized by recording its infrared and NMR spectra. The single crystals used in X-ray diffraction studies were grown in ethanolic solution by slow evaporation at room temperature.

S3. Refinement

The H atom of the NH group was located in a difference map and its position was refined. The other H atoms were positioned with idealized geometry using a riding model [C—H = 0.93–0.96 Å]. All H atoms were refined with isotropic displacement parameters (set to 1.2 times of the U_{eq} of the parent atom) or $U_{iso}(H) = 1.5 U_{eq}$ for methyl groups.

To improve considerably the values of R1, wR2, and GOOF these four reflections (-6 1 0, -2 3 5, 1 5 1, -2 -2 9) were omitted from the refinement.

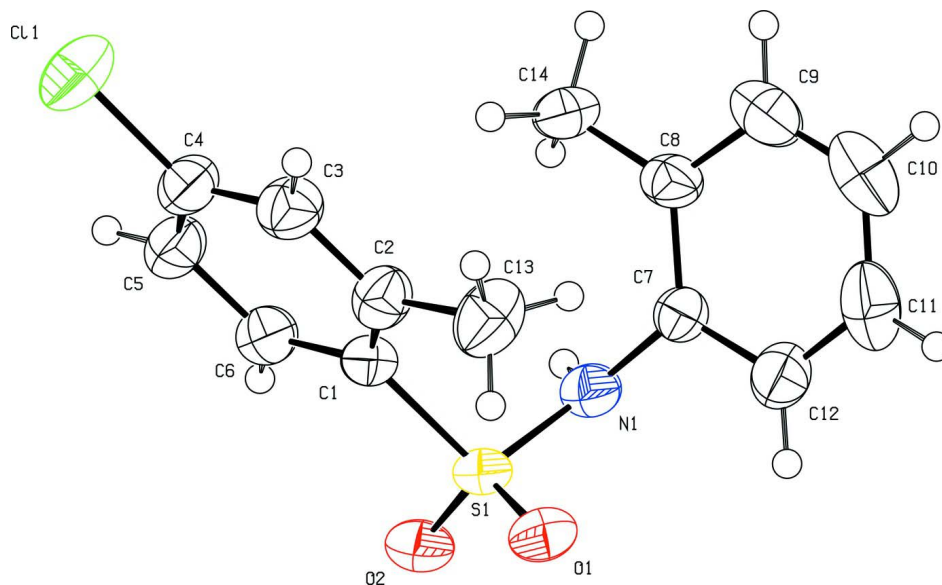


Figure 1

Molecular structure of the title compound showing the atom labeling scheme. The displacement ellipsoids are drawn at the 50% probability level. The H atoms are represented as small spheres of arbitrary radii.

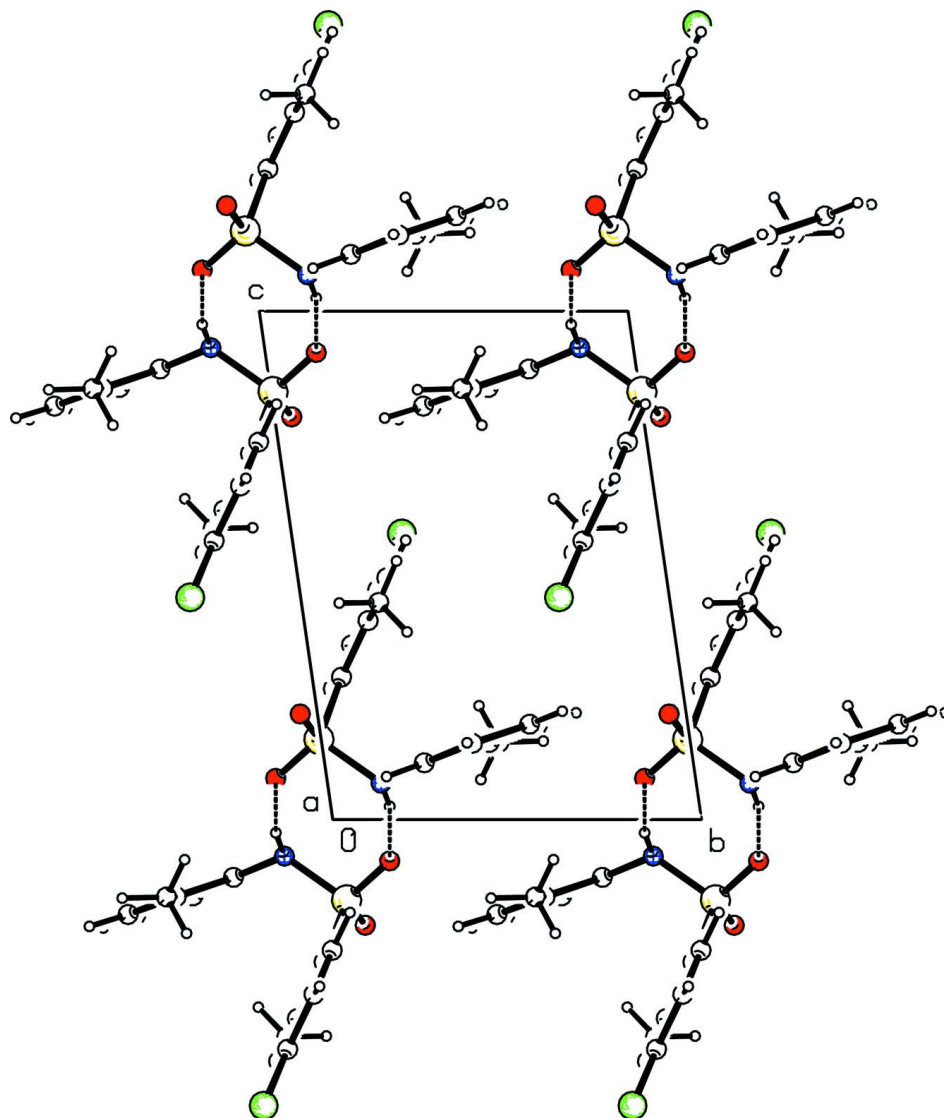


Figure 2

Molecular packing of of the title compound with hydrogen bonding shown as dashed lines.

4-Chloro-2-methyl-N-(2-methylphenyl)benzenesulfonamide

Crystal data

$C_{14}H_{14}ClNO_2S$

$M_r = 295.77$

Triclinic, $P\bar{1}$

Hall symbol: $-P\ 1$

$a = 8.1200$ (8) Å

$b = 8.1832$ (8) Å

$c = 10.985$ (1) Å

$\alpha = 95.81$ (1)°

$\beta = 96.92$ (1)°

$\gamma = 106.82$ (1)°

$V = 686.46$ (11) Å³

$Z = 2$

$F(000) = 308$

$D_x = 1.431$ Mg m⁻³

Cu $K\alpha$ radiation, $\lambda = 1.54180$ Å

Cell parameters from 25 reflections

$\theta = 5.7\text{--}25.2^\circ$

$\mu = 3.86$ mm⁻¹

$T = 299$ K

Prism, colourless

$0.50 \times 0.48 \times 0.18$ mm

Data collection

Enraf–Nonius CAD-4 diffractometer	2366 independent reflections 2194 reflections with $I > 2\sigma(I)$
Radiation source: fine-focus sealed tube	$R_{\text{int}} = 0.054$
Graphite monochromator	$\theta_{\text{max}} = 66.9^\circ$, $\theta_{\text{min}} = 4.1^\circ$
$\omega/2\theta$ scans	$h = -9 \rightarrow 1$
Absorption correction: psi-scan (North <i>et al.</i> , 1968)	$k = -9 \rightarrow 9$
$T_{\text{min}} = 0.228$, $T_{\text{max}} = 0.500$	$l = -13 \rightarrow 13$
2572 measured reflections	3 standard reflections every 120 min intensity decay: 2.5%

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)] = 0.072$	$w = 1/[\sigma^2(F_o^2) + (0.1867P)^2 + 0.2192P]$
$wR(F^2) = 0.235$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.10$	$(\Delta/\sigma)_{\text{max}} = 0.003$
2366 reflections	$\Delta\rho_{\text{max}} = 0.82 \text{ e } \text{\AA}^{-3}$
178 parameters	$\Delta\rho_{\text{min}} = -0.63 \text{ e } \text{\AA}^{-3}$
0 restraints	Extinction correction: <i>SHELXL97</i> (Sheldrick, 2008), $F_c^* = kFc[1 + 0.001x \text{Fc}^2 \lambda^3 / \sin(2\theta)]^{-1/4}$
Primary atom site location: structure-invariant direct methods	Extinction coefficient: 0.020 (4)
Secondary atom site location: difference Fourier map	

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.

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 $F^2 > \sigma(F^2)$ 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 (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Cl1	0.35649 (13)	0.29943 (14)	0.56281 (9)	0.0698 (5)
S1	0.70711 (9)	-0.00610 (8)	0.15793 (6)	0.0388 (4)
O1	0.8587 (3)	-0.0468 (3)	0.2078 (2)	0.0511 (6)
O2	0.5669 (3)	-0.1383 (3)	0.0812 (2)	0.0518 (7)
N1	0.7667 (3)	0.1454 (3)	0.0718 (2)	0.0408 (6)
H1N	0.678 (5)	0.160 (5)	0.026 (3)	0.049*
C1	0.6176 (4)	0.0795 (4)	0.2802 (3)	0.0381 (7)
C2	0.7184 (4)	0.1738 (4)	0.3914 (3)	0.0446 (8)
C3	0.6322 (5)	0.2414 (4)	0.4757 (3)	0.0492 (8)
H3	0.6954	0.3075	0.5496	0.059*
C4	0.4541 (5)	0.2123 (4)	0.4518 (3)	0.0471 (8)
C5	0.3557 (4)	0.1194 (4)	0.3436 (3)	0.0483 (8)
H5	0.2361	0.1015	0.3284	0.058*
C6	0.4388 (4)	0.0529 (4)	0.2572 (3)	0.0445 (7)

H6	0.3743	-0.0105	0.1828	0.053*
C7	0.9159 (4)	0.2918 (4)	0.1137 (2)	0.0370 (7)
C8	0.8982 (4)	0.4545 (4)	0.1516 (3)	0.0417 (7)
C9	1.0502 (6)	0.5921 (4)	0.1866 (3)	0.0580 (9)
H9	1.0420	0.7016	0.2100	0.070*
C10	1.2117 (6)	0.5710 (5)	0.1876 (4)	0.0654 (11)
H10	1.3113	0.6648	0.2132	0.078*
C11	1.2262 (5)	0.4090 (6)	0.1501 (4)	0.0655 (11)
H11	1.3357	0.3943	0.1511	0.079*
C12	1.0791 (5)	0.2706 (5)	0.1118 (3)	0.0516 (8)
H12	1.0889	0.1629	0.0846	0.062*
C13	0.9139 (5)	0.2097 (6)	0.4271 (3)	0.0607 (10)
H13A	0.9401	0.1025	0.4258	0.073*
H13B	0.9513	0.2741	0.5088	0.073*
H13C	0.9736	0.2753	0.3691	0.073*
C14	0.7233 (5)	0.4810 (4)	0.1522 (4)	0.0570 (10)
H14A	0.6460	0.4174	0.0787	0.068*
H14B	0.7352	0.6015	0.1546	0.068*
H14C	0.6767	0.4410	0.2239	0.068*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C11	0.0723 (8)	0.0846 (8)	0.0629 (7)	0.0384 (6)	0.0258 (5)	-0.0018 (5)
S1	0.0430 (6)	0.0280 (5)	0.0466 (5)	0.0131 (3)	0.0107 (3)	-0.0002 (3)
O1	0.0554 (14)	0.0426 (12)	0.0650 (14)	0.0270 (10)	0.0156 (11)	0.0088 (10)
O2	0.0570 (15)	0.0327 (11)	0.0614 (14)	0.0106 (10)	0.0117 (11)	-0.0058 (9)
N1	0.0440 (15)	0.0362 (13)	0.0422 (13)	0.0137 (11)	0.0079 (10)	-0.0001 (10)
C1	0.0431 (17)	0.0308 (14)	0.0427 (15)	0.0129 (11)	0.0114 (12)	0.0052 (11)
C2	0.0422 (18)	0.0510 (17)	0.0449 (16)	0.0191 (13)	0.0091 (13)	0.0103 (13)
C3	0.052 (2)	0.0490 (18)	0.0446 (16)	0.0155 (14)	0.0073 (14)	-0.0003 (13)
C4	0.053 (2)	0.0497 (18)	0.0484 (17)	0.0255 (15)	0.0195 (14)	0.0119 (14)
C5	0.0429 (18)	0.0519 (18)	0.0543 (18)	0.0202 (14)	0.0119 (14)	0.0052 (14)
C6	0.0441 (18)	0.0426 (16)	0.0473 (16)	0.0147 (13)	0.0081 (13)	0.0037 (12)
C7	0.0427 (16)	0.0365 (14)	0.0328 (13)	0.0119 (12)	0.0113 (11)	0.0043 (10)
C8	0.058 (2)	0.0339 (14)	0.0338 (14)	0.0128 (13)	0.0117 (12)	0.0031 (11)
C9	0.075 (3)	0.0388 (17)	0.0516 (18)	0.0032 (15)	0.0113 (16)	0.0070 (13)
C10	0.059 (2)	0.058 (2)	0.062 (2)	-0.0077 (17)	0.0005 (17)	0.0193 (17)
C11	0.041 (2)	0.082 (3)	0.073 (2)	0.0107 (18)	0.0111 (16)	0.032 (2)
C12	0.049 (2)	0.0553 (19)	0.0581 (19)	0.0217 (15)	0.0186 (15)	0.0146 (15)
C13	0.043 (2)	0.080 (3)	0.0544 (19)	0.0199 (17)	-0.0005 (15)	-0.0072 (17)
C14	0.074 (2)	0.0400 (17)	0.069 (2)	0.0274 (17)	0.0329 (19)	0.0081 (15)

Geometric parameters (Å, °)

C11—C4	1.734 (3)	C7—C12	1.388 (5)
S1—O1	1.427 (2)	C7—C8	1.407 (4)
S1—O2	1.431 (2)	C8—C9	1.390 (5)

S1—N1	1.633 (3)	C8—C14	1.498 (5)
S1—C1	1.778 (3)	C9—C10	1.370 (6)
N1—C7	1.424 (4)	C9—H9	0.9300
N1—H1N	0.87 (4)	C10—C11	1.391 (7)
C1—C6	1.392 (5)	C10—H10	0.9300
C1—C2	1.400 (4)	C11—C12	1.373 (5)
C2—C3	1.389 (5)	C11—H11	0.9300
C2—C13	1.522 (5)	C12—H12	0.9300
C3—C4	1.383 (5)	C13—H13A	0.9600
C3—H3	0.9300	C13—H13B	0.9600
C4—C5	1.366 (5)	C13—H13C	0.9600
C5—C6	1.383 (5)	C14—H14A	0.9600
C5—H5	0.9300	C14—H14B	0.9600
C6—H6	0.9300	C14—H14C	0.9600
O1—S1—O2	119.17 (14)	C8—C7—N1	121.0 (3)
O1—S1—N1	108.06 (14)	C9—C8—C7	117.4 (3)
O2—S1—N1	105.21 (14)	C9—C8—C14	120.8 (3)
O1—S1—C1	109.71 (14)	C7—C8—C14	121.9 (3)
O2—S1—C1	106.93 (14)	C10—C9—C8	121.9 (3)
N1—S1—C1	107.12 (13)	C10—C9—H9	119.1
C7—N1—S1	121.1 (2)	C8—C9—H9	119.1
C7—N1—H1N	118 (2)	C9—C10—C11	119.8 (3)
S1—N1—H1N	112 (3)	C9—C10—H10	120.1
C6—C1—C2	121.0 (3)	C11—C10—H10	120.1
C6—C1—S1	115.7 (2)	C12—C11—C10	120.1 (4)
C2—C1—S1	123.3 (2)	C12—C11—H11	119.9
C3—C2—C1	116.9 (3)	C10—C11—H11	119.9
C3—C2—C13	117.4 (3)	C11—C12—C7	119.8 (3)
C1—C2—C13	125.6 (3)	C11—C12—H12	120.1
C4—C3—C2	121.3 (3)	C7—C12—H12	120.1
C4—C3—H3	119.4	C2—C13—H13A	109.5
C2—C3—H3	119.4	C2—C13—H13B	109.5
C5—C4—C3	121.7 (3)	H13A—C13—H13B	109.5
C5—C4—C11	120.0 (3)	C2—C13—H13C	109.5
C3—C4—C11	118.3 (3)	H13A—C13—H13C	109.5
C4—C5—C6	118.1 (3)	H13B—C13—H13C	109.5
C4—C5—H5	120.9	C8—C14—H14A	109.5
C6—C5—H5	120.9	C8—C14—H14B	109.5
C5—C6—C1	120.9 (3)	H14A—C14—H14B	109.5
C5—C6—H6	119.6	C8—C14—H14C	109.5
C1—C6—H6	119.6	H14A—C14—H14C	109.5
C12—C7—C8	121.0 (3)	H14B—C14—H14C	109.5
C12—C7—N1	118.0 (3)		
O1—S1—N1—C7	-45.5 (2)	C11—C4—C5—C6	179.7 (2)
O2—S1—N1—C7	-173.8 (2)	C4—C5—C6—C1	0.2 (5)
C1—S1—N1—C7	72.7 (2)	C2—C1—C6—C5	0.2 (5)

O1—S1—C1—C6	-152.0 (2)	S1—C1—C6—C5	-177.4 (2)
O2—S1—C1—C6	-21.4 (3)	S1—N1—C7—C12	75.9 (3)
N1—S1—C1—C6	90.9 (2)	S1—N1—C7—C8	-106.4 (3)
O1—S1—C1—C2	30.4 (3)	C12—C7—C8—C9	0.1 (4)
O2—S1—C1—C2	161.0 (3)	N1—C7—C8—C9	-177.5 (3)
N1—S1—C1—C2	-86.6 (3)	C12—C7—C8—C14	178.9 (3)
C6—C1—C2—C3	-1.1 (5)	N1—C7—C8—C14	1.3 (4)
S1—C1—C2—C3	176.3 (2)	C7—C8—C9—C10	-1.6 (5)
C6—C1—C2—C13	179.4 (3)	C14—C8—C9—C10	179.5 (3)
S1—C1—C2—C13	-3.1 (5)	C8—C9—C10—C11	1.5 (6)
C1—C2—C3—C4	1.8 (5)	C9—C10—C11—C12	0.3 (6)
C13—C2—C3—C4	-178.7 (3)	C10—C11—C12—C7	-1.8 (5)
C2—C3—C4—C5	-1.5 (5)	C8—C7—C12—C11	1.6 (5)
C2—C3—C4—C11	179.3 (2)	N1—C7—C12—C11	179.3 (3)
C3—C4—C5—C6	0.5 (5)		

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—H1N \cdots O2 ⁱ	0.87 (4)	2.14 (4)	2.993 (4)	167 (3)

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