organic compounds

(3aR,6S,7aR)-7a-Bromo-2-methyl-sulfonyl-1,2,3,6,7,7a-hexahydro-3a,6-ep-oxyisoindole

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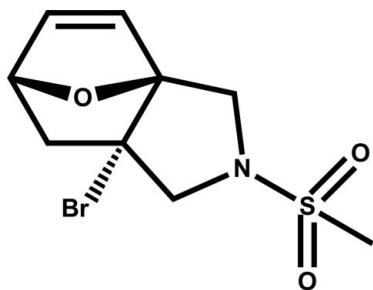Correspondence e-mail: hakan.arslan.acad@gmail.com

In the title compound, $C_9H_{12}BrNO_3S$, the two tetrahydrofuran rings adopt envelope conformations, the pyrrolidine ring adopts a half-chair conformation and the six-membered ring is in a boat conformation. In the crystal, weak intermolecular C—H⋯O hydrogen bonds link the molecules into $R_2^2(8)$ and $R_2^2(14)$ rings along the b-axis direction.

Related literature

For a related structure, see: Koşar et al. (2006). For uses of sulfonamides in medicine, in particular the treatment of bacterial infection, see: Kleemann et al. (1999); Cremlyn (1996). For the synthesis of sulfonamides, see: Anderson (1979). For thermal intramolecular Diels–Alder reaction of furans (IMDAF), see: Demircan & Parsons (2002); Arslan et al. (2008). A mesyl group in the structure is normally chosen as a protective group for nitrogen, but at the same time accelerates the cycloaddition process for IMDAF, see: Greene (1981); Choony et al. (1997). For standard bond lengths, see: Allen et al. (1987). For puckering parameters, see: Cremer & Pople (1975). For graph-set notation, see: Bernstein et al. (1995).

Experimental

Crystal data

$C_9H_{12}BrNO_3S$	γ = 97.812 (9)°
M_r = 294.17	V = 553.46 (10) Å^3
Triclinic, $P\bar{1}$	Z = 2
a = 5.9478 (7) Å	Mo $K\alpha$ radiation
b = 9.5869 (10) Å	μ = 3.89 mm^{-1}
c = 10.7775 (11) Å	T = 296 K
α = 114.307 (8)°	0.38 × 0.23 × 0.08 mm
β = 90.481 (9)°	

Data collection

Stoe IPDS 2 diffractometer	8163 measured reflections
Absorption correction: integration (X-RED32; Stoe & Cie, 2001)	2293 independent reflections
T_{min} = 0.223, T_{max} = 0.682	1920 reflections with $I > 2\sigma(I)$
	R_{int} = 0.082

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.047	137 parameters
$wR(F^2)$ = 0.107	H-atom parameters constrained
S = 1.10	$\Delta\rho_{max}$ = 0.86 e Å^{-3}
2293 reflections	$\Delta\rho_{min}$ = −0.44 e Å^{-3}

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

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
C9—H9A⋯O2^i	0.96	2.59	3.385 (7)	140
C9—H9C⋯O1^{ii}	0.96	2.59	3.540 (6)	172

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

Data collection: X-AREA (Stoe & Cie, 2002); cell refinement: X-AREA; data reduction: X-RED32 (Stoe & Cie, 2001); program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: OLEX2 (Dolomanov et al., 2009); software used to prepare material for publication: SHELXTL (Sheldrick, 2008), OLEX2, publCIF (Westrip, 2010) and Mercury (Macrae et al., 2006).

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supporting information

(3a*R*,6*S*,7a*R*)-7a-Bromo-2-methylsulfonyl-1,2,3,6,7,7a-hexahydro-3a,6-epoxy-isoindole

Ersin Temel, Aydın Demircan, Hakan Arslan and Orhan Büyükgüngör

S1. Comment

Sulfonamides are one of the most important groups of compounds for the medical purposes (Kleemann *et al.*, 1999). They have mostly been applied for the treatment of bacterial infection (Cremlyn, 1996). Sulfonamide is not only an early class of antibiotics, also, has showed different functionality such as a protease inhibitor amprenavir, the analgesic celecoxib, sildenafil for erectile dysfunction, and the antimigraine agent sumatriptan. The most sulfonamides have been synthesized from a reaction between a sulfonyl chloride and ammonia or primary or secondary amines or *via* related transformations (Anderson, 1979).

Several thermal intramolecular Diels Alder reaction of furans (IMDAF) cycloadditon were performed including a nitrogen linked side chain of furan and already reported by Demircan and his co-workers (Demircan and Parsons, 2002; Arslan *et al.*, 2008). We would like to report here a newly synthesized sulfonamide, I.

In continuation of our interest, mesyl group in the structure is normally chosen as a protective group for nitrogen, but at the same time, accelerates the cycloaddition process for IMDAF (Greene, 1981; Choony *et al.*, 1997). This facile, versatile and environmentally friendly reaction was accomplished in aqueous condition and stirred for two days at 372 K.

The molecular structure of the title compound, I, is shown in Fig. 1. A l l bond lengths show normal values (Allen *et al.*, 1987). In addition, the C—Br bond distance, 1.953 (4) Å, is not significantly different from the value reported for C—Br single bond (1.961 (3) Å; Koşar *et al.*, 2006). The six membered ring, C1—C6, is in a boat conformation with puckering parameter $Q = 0.933$ (5) Å, $\theta = 89.1$ (3) °, $\varphi = 119.1$ (3) °. The tetrahydrofuran, O1/C3–C6, and bromo-attached tetrahydrofuran, O1/C3/C2/C1/C6, rings adopt envelope conformations, and the puckering parameter Q values are 0.517 (5) and 0.607 (4) ° Å, respectively (Cremer & Pople, 1975). The pyrrolidine ring, N1/C7/C6/C1/C8, adopts half chair conformation, and the puckering parameter $Q = 0.368$ (4) Å and $\varphi = 304.8$ (7) °, (Cremer & Pople, 1975).

Fig. 2 shows the packing of the molecules in the unit cell. The crystal packing of (I) is stabilized by intermolecular C9—H9A⋯O2 and C9—H9C⋯O1 interactions (Table 1). The methyl group in the reference molecule at (x, y, z) acts as double hydrogen bond donor, *via* H9A and H9C, to atoms O2 in the molecule at (-x + 2, -y + 2, -z + 2) and O1 in the molecule at (-x + 2, -y + 1, -z + 2), so forming successive $R_2^2(8)$ and $R_2^2(14)$ rings running parallel to the [010] direction (Bernstein *et al.*, 1995).

S2. Experimental

N-(2-bromoprop-2-en-1-yl)-*N*-(2-furylmethyl)methanesulfonamide, II, (1 g, 3.4 mmol) was stirred in water (25 ml) at 372 K for two days (Fig. 3). The reaction was stirred and monitored by thin layer chromatography until no further cycloadditon observed. The mixture was poured into ethylacetate (25 ml) and aqueous phase was washed with excess of ethyl acetate (2 *x* 25 ml). Combined organic phases was dried on magnesium sulfate and filtered off. The solvent was then removed under reduced pressure. The residue was subjected to flash column chromatography to afford the title

compound, (3a*R*,6*S*,7a*R*)-7a-bromo-2-(methylsulfonyl)-1,2,3,6,7,7a-hexahydro-3a,6-epoxyisoindole, **I**, with 0.74 g, 74% yield as light brown crystals.

S3. Refinement

H atoms were positioned geometrically and treated using a riding model, fixing the bond lengths at 0.96, 0.97, 0.98 and 0.93 Å for CH$_3$, CH$_2$, CH and CH(aromatic), respectively. The displacement parameters of the H atoms were constrained with U_{iso}(H) = 1.2U_{eq} (aromatic, methylene or methine C) or 1.5U_{eq} (methyl C).
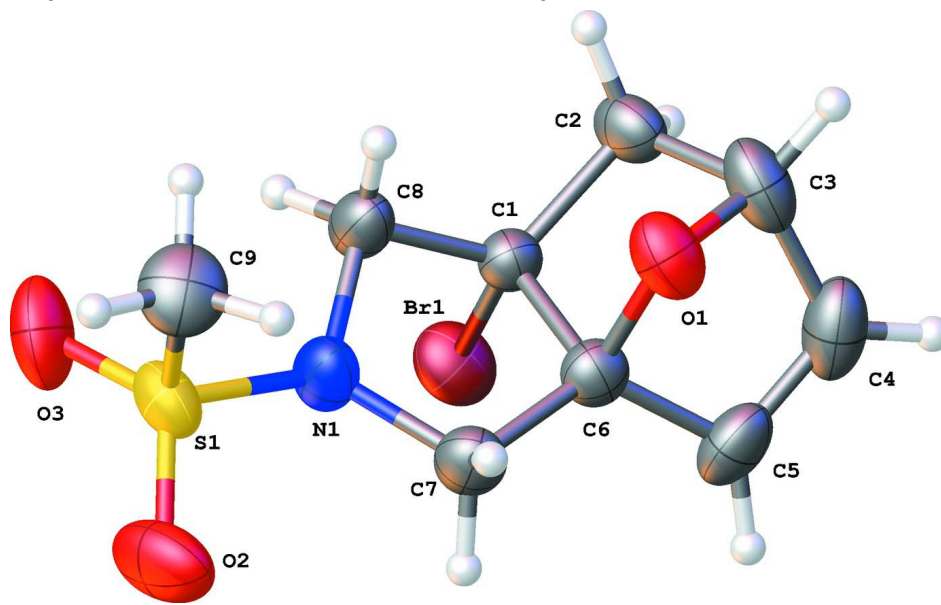
Figure 1

The molecular structure of the title compound, with displacement ellipsoids drawn at the 30% probability level.
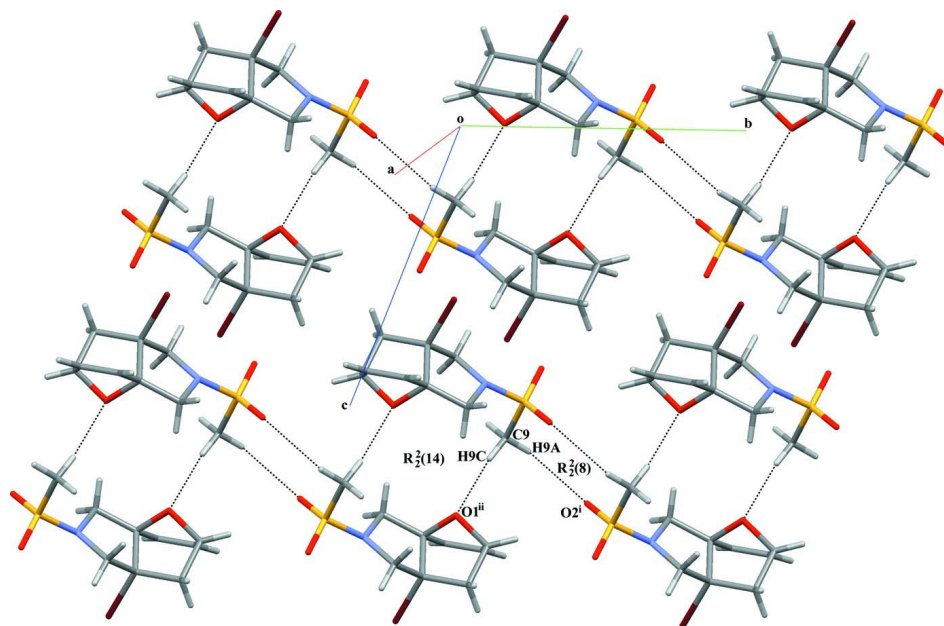
Figure 2

Part of the crystal structure of the title compound, showing the formation of $R^2_2(8)$ and $R^2_2(14)$ rings along [010]. Hydrogen bonds are indicated by dashed lines. (Symmetry codes as in Table 1)
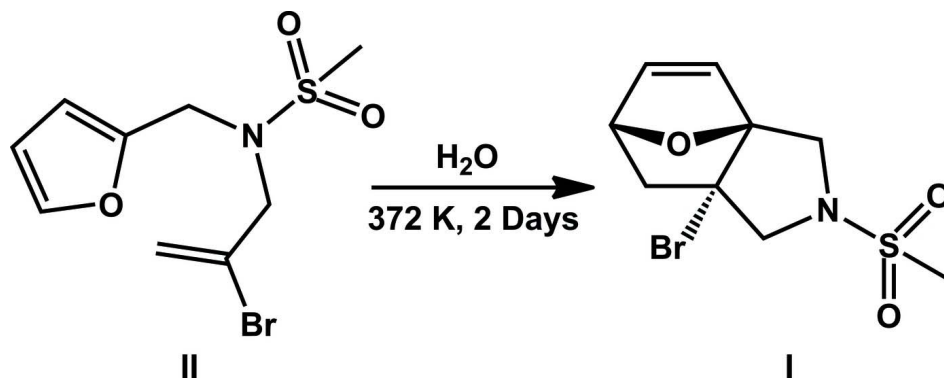
Figure 3

Synthesis of the title compound.

(3a*R*,6*S*,7a*R*)-7a-Bromo-2-methylsulfonyl-1,2,3,6,7,7a- hexahydro-3a,6-epoxyisoindole

Crystal data

$C_9H_{12}BrNO_3S$	$Z = 2$
$M_r = 294.17$	$F(000) = 296$
Triclinic, $P\overline{1}$	$D_x = 1.765$ Mg m^{-3}
Hall symbol: -P 1	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 5.9478$ (7) Å	Cell parameters from 8163 reflections
$b = 9.5869$ (10) Å	$\theta = 2.1–27.5°$
$c = 10.7775$ (11) Å	$\mu = 3.89$ mm^{-1}
$\alpha = 114.307$ (8)°	$T = 296$ K
$\beta = 90.481$ (9)°	Block, light-brown
$\gamma = 97.812$ (9)°	$0.38 \times 0.23 \times 0.08$ mm
$V = 553.46$ (10) Å^3	

Data collection

Stoe IPDS 2 diffractometer	8163 measured reflections
Radiation source: fine-focus sealed tube	2293 independent reflections
Graphite monochromator	1920 reflections with $I > 2\sigma(I)$
Detector resolution: 6.67 pixels mm⁻¹	$R_{int} = 0.082$
rotation method scans	$\theta_{max} = 26.5°$, $\theta_{min} = 2.1°$
Absorption correction: integration	$h = -7 \rightarrow 7$
(*X-RED*; Stoe & Cie, 2001)	$k = -12 \rightarrow 12$
$T_{min} = 0.223$, $T_{max} = 0.682$	$l = -13 \rightarrow 13$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.047$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.107$	
$S = 1.10$	H-atom parameters constrained
2293 reflections	$w = 1/[\sigma^2(F_o^2) + (0.0452P)^2 + 0.3277P]$
137 parameters	where $P = (F_o^2 + 2F_c^2)/3$
0 restraints	$(\Delta/\sigma)_{max} < 0.001$
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{max} = 0.86$ e Å⁻³
	$\Delta\rho_{min} = -0.44$ 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.

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 (Å²)

	x	*y*	*z*	$U_{iso}*/U_{eq}$
C1	0.7380 (6)	0.3068 (4)	0.6385 (4)	0.0348 (8)
C2	0.8248 (7)	0.1507 (5)	0.5964 (4)	0.0438 (9)
H2A	0.9770	0.1543	0.5651	0.053*
H2B	0.7234	0.0668	0.5264	0.053*
C3	0.8218 (9)	0.1363 (5)	0.7338 (5)	0.0553 (11)
H3	0.9189	0.0654	0.7421	0.066*
C4	0.5780 (9)	0.1066 (6)	0.7645 (5)	0.0577 (12)
H4	0.4995	0.0132	0.7588	0.069*
C5	0.4970 (8)	0.2380 (6)	0.8007 (4)	0.0502 (10)
H5	0.3516	0.2569	0.8268	0.060*
C6	0.6907 (6)	0.3509 (4)	0.7910 (4)	0.0369 (8)
C7	0.7123 (7)	0.5249 (5)	0.8604 (4)	0.0441 (9)
H7A	0.5645	0.5578	0.8801	0.053*
H7B	0.8083	0.5663	0.9446	0.053*
C8	0.9051 (7)	0.4468 (4)	0.6497 (4)	0.0429 (9)
H8A	1.0585	0.4388	0.6744	0.051*

H8B	0.9039	0.4590	0.5647	0.051*
O2	0.7873 (6)	0.8440 (4)	0.8963 (4)	0.0738 (11)
Br1	0.46555 (8)	0.29243 (5)	0.52887 (5)	0.05052 (17)
N1	0.8186 (6)	0.5743 (4)	0.7581 (3)	0.0443 (8)
O1	0.8850 (5)	0.2972 (3)	0.8292 (3)	0.0484 (7)
C9	1.2003 (8)	0.7824 (6)	0.8803 (5)	0.0592 (12)
H9A	1.2643	0.8899	0.9136	0.089*
H9B	1.2967	0.7208	0.8158	0.089*
H9C	1.1881	0.7529	0.9552	0.089*
O3	0.9632 (6)	0.7717 (4)	0.6764 (4)	0.0633 (9)
S1	0.92989 (17)	0.75291 (11)	0.80041 (11)	0.0423 (2)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0378 (18)	0.034 (2)	0.0349 (19)	0.0078 (15)	0.0081 (15)	0.0151 (15)
C2	0.044 (2)	0.030 (2)	0.053 (2)	0.0081 (16)	0.0068 (18)	0.0124 (17)
C3	0.075 (3)	0.036 (2)	0.059 (3)	0.012 (2)	−0.007 (2)	0.022 (2)
C4	0.083 (3)	0.044 (3)	0.047 (2)	−0.008 (2)	0.002 (2)	0.024 (2)
C5	0.055 (2)	0.055 (3)	0.039 (2)	−0.003 (2)	0.0134 (19)	0.021 (2)
C6	0.0406 (19)	0.038 (2)	0.0328 (19)	0.0069 (15)	0.0043 (15)	0.0146 (16)
C7	0.052 (2)	0.036 (2)	0.041 (2)	0.0093 (17)	0.0121 (17)	0.0124 (17)
C8	0.052 (2)	0.031 (2)	0.043 (2)	0.0058 (17)	0.0165 (18)	0.0135 (17)
O2	0.066 (2)	0.0383 (19)	0.098 (3)	0.0125 (16)	0.012 (2)	0.0082 (18)
Br1	0.0549 (3)	0.0520 (3)	0.0448 (2)	0.01178 (18)	−0.00663 (17)	0.01939 (19)
N1	0.057 (2)	0.0296 (18)	0.0427 (19)	0.0044 (14)	0.0115 (15)	0.0122 (14)
O1	0.0595 (18)	0.0385 (16)	0.0455 (16)	0.0081 (13)	−0.0092 (13)	0.0159 (13)
C9	0.051 (2)	0.067 (3)	0.058 (3)	0.002 (2)	−0.011 (2)	0.027 (3)
O3	0.082 (2)	0.053 (2)	0.067 (2)	−0.0026 (16)	−0.0173 (18)	0.0413 (18)
S1	0.0465 (6)	0.0280 (5)	0.0509 (6)	0.0065 (4)	−0.0034 (4)	0.0148 (4)

Geometric parameters (Å, º)

C1—C8	1.519 (5)	C6—C7	1.507 (6)
C1—C2	1.538 (5)	C7—N1	1.482 (5)
C1—C6	1.558 (5)	C7—H7A	0.9700
C1—Br1	1.953 (4)	C7—H7B	0.9700
C2—C3	1.542 (6)	C8—N1	1.460 (5)
C2—H2A	0.9700	C8—H8A	0.9700
C2—H2B	0.9700	C8—H8B	0.9700
C3—O1	1.452 (5)	O2—S1	1.422 (4)
C3—C4	1.505 (7)	N1—S1	1.619 (3)
C3—H3	0.9800	C9—S1	1.749 (5)
C4—C5	1.317 (7)	C9—H9A	0.9600
C4—H4	0.9300	C9—H9B	0.9600
C5—C6	1.506 (6)	C9—H9C	0.9600
C5—H5	0.9300	O3—S1	1.432 (3)
C6—O1	1.448 (5)		

C8—C1—C2	118.5 (3)	C7—C6—C1	107.2 (3)
C8—C1—C6	101.3 (3)	N1—C7—C6	103.0 (3)
C2—C1—C6	102.7 (3)	N1—C7—H7A	111.2
C8—C1—Br1	108.7 (3)	C6—C7—H7A	111.2
C2—C1—Br1	112.9 (3)	N1—C7—H7B	111.2
C6—C1—Br1	112.0 (2)	C6—C7—H7B	111.2
C1—C2—C3	100.0 (3)	H7A—C7—H7B	109.1
C1—C2—H2A	111.8	N1—C8—C1	102.6 (3)
C3—C2—H2A	111.8	N1—C8—H8A	111.2
C1—C2—H2B	111.8	C1—C8—H8A	111.2
C3—C2—H2B	111.8	N1—C8—H8B	111.2
H2A—C2—H2B	109.5	C1—C8—H8B	111.2
O1—C3—C4	100.7 (4)	H8A—C8—H8B	109.2
O1—C3—C2	101.0 (3)	C8—N1—C7	111.4 (3)
C4—C3—C2	108.5 (4)	C8—N1—S1	121.6 (3)
O1—C3—H3	115.0	C7—N1—S1	120.8 (3)
C4—C3—H3	115.0	C6—O1—C3	95.6 (3)
C2—C3—H3	115.0	S1—C9—H9A	109.5
C5—C4—C3	107.0 (4)	S1—C9—H9B	109.5
C5—C4—H4	126.5	H9A—C9—H9B	109.5
C3—C4—H4	126.5	S1—C9—H9C	109.5
C4—C5—C6	105.1 (4)	H9A—C9—H9C	109.5
C4—C5—H5	127.4	H9B—C9—H9C	109.5
C6—C5—H5	127.4	O2—S1—O3	119.5 (2)
O1—C6—C5	101.4 (3)	O2—S1—N1	105.8 (2)
O1—C6—C7	111.1 (3)	O3—S1—N1	107.14 (19)
C5—C6—C7	125.8 (4)	O2—S1—C9	109.3 (3)
O1—C6—C1	97.9 (3)	O3—S1—C9	106.7 (2)
C5—C6—C1	109.8 (3)	N1—S1—C9	107.9 (2)
C8—C1—C2—C3	108.2 (4)	C5—C6—C7—N1	−143.5 (4)
C6—C1—C2—C3	−2.3 (4)	C1—C6—C7—N1	−12.1 (4)
Br1—C1—C2—C3	−123.1 (3)	C2—C1—C8—N1	−148.4 (4)
C1—C2—C3—O1	−35.0 (4)	C6—C1—C8—N1	−37.1 (4)
C1—C2—C3—C4	70.3 (4)	Br1—C1—C8—N1	80.9 (3)
O1—C3—C4—C5	31.9 (5)	C1—C8—N1—C7	32.5 (4)
C2—C3—C4—C5	−73.6 (5)	C1—C8—N1—S1	−175.0 (3)
C3—C4—C5—C6	0.7 (5)	C6—C7—N1—C8	−12.6 (5)
C4—C5—C6—O1	−33.4 (4)	C6—C7—N1—S1	−165.3 (3)
C4—C5—C6—C7	−160.2 (4)	C5—C6—O1—C3	51.1 (4)
C4—C5—C6—C1	69.4 (4)	C7—C6—O1—C3	−173.0 (3)
C8—C1—C6—O1	−84.1 (3)	C1—C6—O1—C3	−61.0 (3)
C2—C1—C6—O1	38.8 (3)	C4—C3—O1—C6	−50.1 (4)
Br1—C1—C6—O1	160.2 (2)	C2—C3—O1—C6	61.4 (4)
C8—C1—C6—C5	170.7 (3)	C8—N1—S1—O2	173.3 (4)
C2—C1—C6—C5	−66.4 (4)	C7—N1—S1—O2	−36.8 (4)
Br1—C1—C6—C5	55.0 (4)	C8—N1—S1—O3	44.7 (4)

C8—C1—C6—C7	31.0 (4)	C7—N1—S1—O3	−165.3 (3)
C2—C1—C6—C7	153.9 (3)	C8—N1—S1—C9	−69.8 (4)
Br1—C1—C6—C7	−84.7 (3)	C7—N1—S1—C9	80.1 (4)
O1—C6—C7—N1	93.8 (4)		

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C9—H9*A*···O2[i]	0.96	2.59	3.385 (7)	140
C9—H9*C*···O1[ii]	0.96	2.59	3.540 (6)	172

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