The crystal structure of 2-[5-(dimethyl-amino)naphthalene-1-sulfonamido]-phenyl 5-(dimethylamino)naphthalene-1-sulfonate

Kittipong Chainok,[a] Tanwawan Duangthongyou,[b] Thawatchai Tuntulani,[c] Apinya Chuenka[d] and Boontana Wannalerse[d]*

[a]Department of Physics, Faculty of Science and Technology, Thammasat University, Khlong Luang, Pathum Thani, 12120, Thailand, [b]Department of Chemistry, Faculty of Science, Kasetsart University, Bangkok 10903, Thailand, [c]Supramolecular Chemistry Research Unit, Department of Chemistry, Faculty of Science, Chulalongkorn University, Bangkok 10330, Thailand, and [d]Department of Chemistry and Center of Excellence for Innovation in Chemistry, Faculty of Science, Kasetsart University, Bangkok 10903, Thailand. *Correspondence e-mail: fscibnw@ku.ac.th

The complete molecule of the title compound, $C_{30}H_{29}N_3O_5S_2$, is generated by a crystallographic twofold axis: the O atom and NH group attached to the central benzene ring are statistically disordered. The dihedral angle between the naphthalene ring system and the central benzene ring is 52.99 (6)°, while the pendant naphthalene ring systems subtend a dihedral angle of 68.17 (4)°. An intramolecular C—H···O hydrogen bond closes an S(6) ring. In the crystal, the molecules are linked by weak C—H···O hydrogen bonds.

1. Related literature

For the use of dansyl tags to monitor biological activity in enzyme systems, see: Brown *et al.* (1970); Liu *et al.* (2010). Dansyl-conjugated liposome has been used to modulate the fluorescence resonance energy transfer (FRET) mechanism, see: Li *et al.* (2006). Dansyl fluorogenic sensors have been used for the recognition and detection of targets such as cationic and anionic species, see: Cao *et al.* (2014); Jisha *et al.* (2009); Bhalla *et al.* (2007). For crystal structures of dansyl derivatives, see: Bhatt *et al.* (2011); Zhang *et al.* (2009) and of metal–calix[4]arene complexes bearing two dansyl carboxamide units, see: Buie *et al.* (2008).
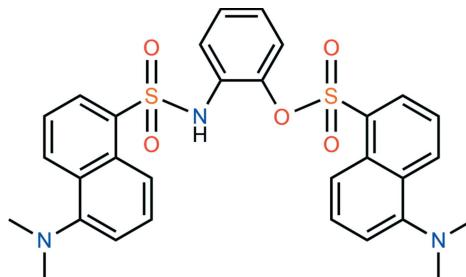
2. Experimental

2.1. Crystal data

$C_{30}H_{29}N_3O_5S_2$
$M_r = 575.68$
Monoclinic, $C2/c$
$a = 12.7594 (13)$ Å
$b = 13.3481 (14)$ Å
$c = 16.4331 (17)$ Å
$\beta = 98.349 (4)°$

$V = 2769.1 (5)$ Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 0.24$ mm^{-1}
$T = 296$ K
$0.26 \times 0.22 \times 0.22$ mm

2.2. Data collection

Bruker D8 QUEST CMOS diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2014)
$T_{min} = 0.698$, $T_{max} = 0.746$

17644 measured reflections
3444 independent reflections
2246 reflections with $I > 2\sigma(I)$
$R_{int} = 0.041$

2.3. Refinement

$R[F^2 > 2\sigma(F^2)] = 0.047$
$wR(F^2) = 0.113$
$S = 1.03$
3444 reflections

186 parameters
H-atom parameters constrained
$\Delta\rho_{max} = 0.26$ e Å^{-3}
$\Delta\rho_{min} = -0.23$ e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
C7—H7···O3[i]	0.93	2.37	3.030 (2)	128
C13—H13···O3[i]	0.93	2.73	3.386 (2)	129

Symmetry code: (i) $-x + \frac{3}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$.

Data collection: *APEX2* (Bruker, 2014); cell refinement: *SAINT* (Bruker, 2014); data reduction: *SAINT*; program(s) used to solve structure: *SHELXT* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015b); molecular graphics: *OLEX2* (Dolomanov *et al.*, 2009); software used to prepare material for publication: *OLEX2*.

Acknowledgements

data reports

References

Bhalla, V., Kumar, R., Kumar, M. & Dhir, A. (2007). *Tetrahedron*, **63**, 11153–11159.

Bhatt, P., Govender, T., Kruger, H. G. & Maguire, G. E. M. (2011). *Acta Cryst.* E**67**, o2458–o2459.

Brown, C. S. & Cunningham, L. W. (1970). *Biochemistry*, **9**, 3878–3885.

Bruker (2014). *APEX2*, *SADABS* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.

Buie, N. M., Talanov, V. S., Butcher, R. J. & Talanova, G. G. (2008). *Inorg. Chem.* **47**, 3549–3558.

Cao, Y., Ding, L., Wang, S., Liu, Y., Fan, J., Hu, W., Liu, P. & Fang, Y. (2014). *Appl. Mater. Interfaces*, **6**, 49–56.

Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K. & Puschmann, H. (2009). *J. Appl. Cryst.* **42**, 339–341.

Jisha, V. S., Thomas, A. J. & Ramaiah, D. (2009). *J. Org. Chem.* **74**, 6667–6673.

Li, X., McCarroll, M. & Kohli, P. (2006). *Langmuir*, **22**(21), 8165–8167.

Liu, C.-Y., Guo, C. W., Chang, Y. F., Wang, J.-T., Shih, H.-W., Hsu, Y.-F., Chen, C.-W., Chen, S.-K., Wang, Y.-C., Cheng, T. J., Ma, C., Wong, C.-H., Fang, J.-M. & Cheng, W.-C. (2010). *Org. Lett.* **12**, 1608–1611.

Sheldrick, G. M. (2015a). *Acta Cryst.* A**71**, 3–8.

Sheldrick, G. M. (2015b). *Acta Cryst.* C**71**, 3–8.

Zhang, S., Zhao, B., Su, Z., Xia, X. & Zhang, Y. (2009). *Acta Cryst.* E**65**, o1452.

supporting information

The crystal structure of 2-[5-(dimethylamino)naphthalene-1-sulfonamido]phenyl 5-(dimethylamino)naphthalene-1-sulfonate

Kittipong Chainok, Tanwawan Duangthongyou, Thawatchai Tuntulani, Apinya Chuenka and Boontana Wannalerse

S1. Introduction

Dansyl derivatives can be widely used as fluorescence probes in biological and environmental systems. Dansyl tags have been increasingly used to monitor biological activities in the enzyme system for providing the accurate information (Brown *et al.*, 1970; Liu *et al.*, 2010). An example is dansyl-conjugated liposome for modulating fluorescence resonance energy transfer (FRET) mechanism (Li *et al.* 2006). Furthermore, dansyl fluorogenic sensors were prepared for recognition and detection of many targets such as cationic and anionic species (Cao *et al.*, 2014; Jisha *et al.*, 2009; Bhalla *et al.*, 2007). Crystal structures of dansyl derivatives (Bhatt *et al.*, 2011; Zhang *et al.*, 2009) and metal complexes of calix[4]arene bearing two dansyl carboxamide units have been reported (Buie *et al.*, 2008).

S2. Synthesis and crystallization

The title compound was synthesized by condensation of 2-aminophenol (0.55 g, 5.04 mmol) and dansyl chloride (2.72 g, 10.08 mmol) using potassium carbonate (17.27 g, 12.50 mmol) as a base in acetonitrile (30 ml). The solution was heated and stirred under N_2 atmosphere for 24 h. The solvent was then removed by a rotary evaporator. Water (10 ml) was added to the residue and the organic phase was extracted with dichloromethane (3 x 20 ml). The organic layer was dried with Na_2SO_4. The product was purified by column chromatography using dichloromethane as an eluent. The solvent was evaporated to afford a yellow crystalline solid in 55% yield. Single crystals suitable for X-ray measurements were obtained by recrystallization using the mixture solution of dichloromethane and hexane (1:1, *v/v*) at room temperature.

S3. Refinement

Atom O1 and the N1H1 group attached to the central benzene ring are statistically disordered and were refined with the occupancies of the N, H and O atoms fixed at 0.5. All H atoms were positioned geometrically and refined using a riding model, with C—H = 0.93 Å for aryl and 0.96 Å for methyl H atoms, U_{iso} (H) = $1.2U_{eq}$ (C) for aryl and $1.5U_{eq}$ (C) for methyl H atoms. The N-bound H-atom was refined with N—H = 0.86 Å, and with U_{iso}(H) = $1.2U_{eq}$(N).
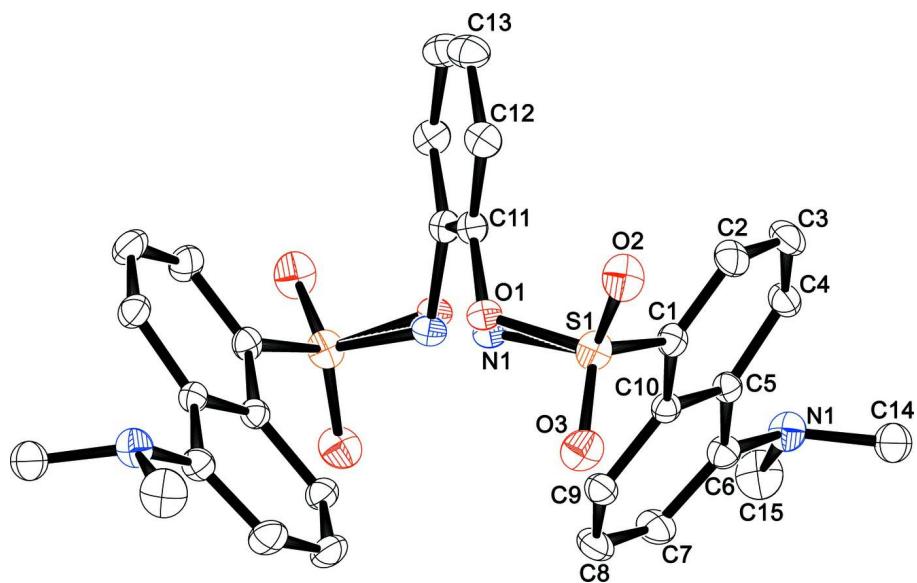
Figure 1

The molecular structure of the title compound with 30% probability ellipsoids and atom numbering. Hydrogen atoms are omitted for clarity.
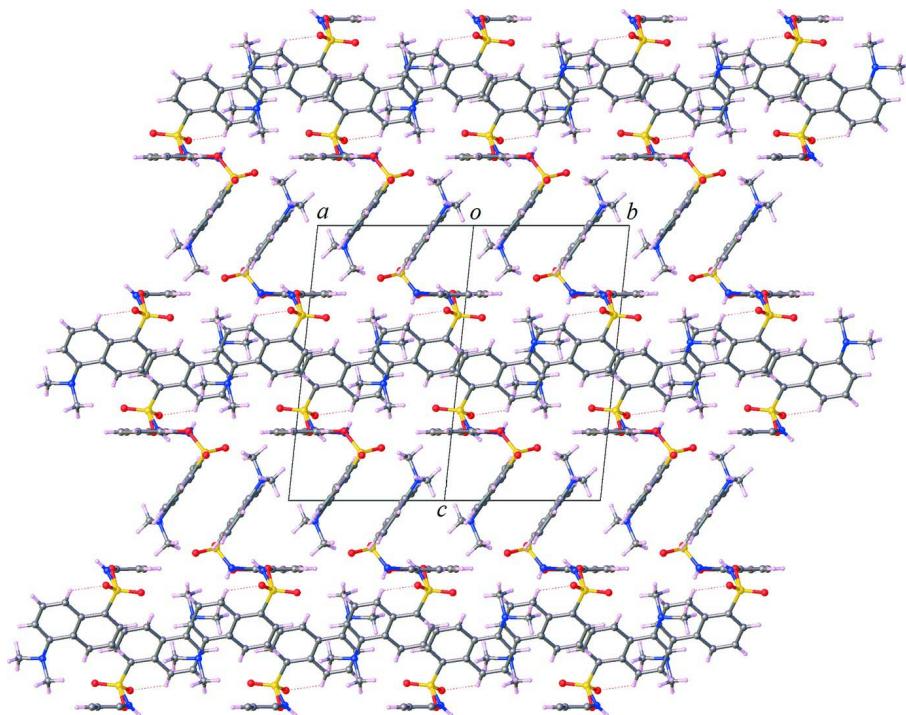

Figure 2

The crystal packing of the title compound, viewed along the [110] direction.

2-[5-(Dimethylamino)naphthalene-1-sulfonamido]phenyl 5-(dimethylamino)naphthalene-1-sulfonate

Crystal data
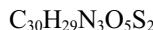
$C_{30}H_{29}N_3O_5S_2$	$F(000) = 1208$
$M_r = 575.68$	$D_x = 1.381$ Mg m^{-3}
Monoclinic, $C2/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 12.7594$ (13) Å	Cell parameters from 4957 reflections
$b = 13.3481$ (14) Å	$\theta = 3.1–25.7°$
$c = 16.4331$ (17) Å	$\mu = 0.24$ mm^{-1}
$\beta = 98.349$ (4)°	$T = 296$ K
$V = 2769.1$ (5) Å^3	Block, light green
$Z = 4$	$0.26 \times 0.22 \times 0.22$ mm

Data collection

Bruker D8 QUEST CMOS diffractometer	$T_{min} = 0.698$, $T_{max} = 0.746$
Radiation source: microfocus sealed x-ray tube, Incoatec Iμus	17644 measured reflections
	3444 independent reflections
GraphiteDouble Bounce Multilayer Mirror monochromator	2246 reflections with $I > 2\sigma(I)$
	$R_{int} = 0.041$
Detector resolution: 10.5 pixels mm^{-1}	$\theta_{max} = 28.3°$, $\theta_{min} = 3.1°$
ω and φ scans	$h = -15 \rightarrow 16$
Absorption correction: multi-scan (*SADABS*; Bruker, 2014)	$k = -17 \rightarrow 17$
	$l = -21 \rightarrow 21$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.047$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.113$	
$S = 1.03$	H-atom parameters constrained
3444 reflections	$w = 1/[\sigma^2(F_o^2) + (0.0488P)^2 + 1.1669P]$ where $P = (F_o^2 + 2F_c^2)/3$
186 parameters	
0 restraints	$(\Delta/\sigma)_{max} < 0.001$
	$\Delta\rho_{max} = 0.26$ 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 (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
S1	0.69732 (3)	0.73580 (4)	0.32645 (3)	0.05431 (17)	
N1	0.603 (2)	0.709 (2)	0.2569 (14)	0.0418 (18)	0.5
H1	0.5801	0.7537	0.2215	0.050*	0.5
O2	0.77825 (10)	0.66139 (12)	0.33521 (10)	0.0736 (5)	
O3	0.72349 (11)	0.83601 (11)	0.30878 (10)	0.0711 (4)	
N2	0.35617 (13)	0.82675 (13)	0.57539 (10)	0.0609 (5)	
C11	0.55450 (13)	0.61136 (13)	0.25005 (10)	0.0433 (4)	

C5	0.49120 (13)	0.77874 (12)	0.49182 (10)	0.0427 (4)	
C6	0.54736 (13)	0.79731 (12)	0.42414 (10)	0.0413 (4)	
C1	0.62854 (13)	0.72779 (13)	0.41220 (11)	0.0450 (4)	
C10	0.40779 (14)	0.84536 (14)	0.50673 (12)	0.0495 (4)	
C12	0.60785 (15)	0.52183 (15)	0.24889 (12)	0.0543 (5)	
H12	0.6806	0.5215	0.2481	0.065*	
C7	0.51636 (15)	0.87928 (13)	0.37174 (11)	0.0500 (4)	
H7	0.5533	0.8940	0.3285	0.060*	
C4	0.51413 (16)	0.69084 (14)	0.53896 (12)	0.0531 (5)	
H4	0.4748	0.6766	0.5810	0.064*	
C2	0.65034 (16)	0.64565 (15)	0.46148 (12)	0.0582 (5)	
H2	0.7046	0.6022	0.4527	0.070*	
C9	0.37880 (17)	0.92039 (15)	0.45129 (13)	0.0612 (5)	
H9	0.3220	0.9615	0.4583	0.073*	
C8	0.43259 (17)	0.93625 (15)	0.38477 (13)	0.0611 (5)	
H8	0.4104	0.9876	0.3480	0.073*	
C13	0.55357 (17)	0.43329 (16)	0.24897 (14)	0.0665 (6)	
H13	0.5895	0.3728	0.2476	0.080*	
C3	0.59130 (17)	0.62698 (15)	0.52481 (13)	0.0635 (6)	
H3	0.6052	0.5702	0.5574	0.076*	
C14	0.41854 (19)	0.83896 (17)	0.65611 (13)	0.0707 (6)	
H14A	0.4905	0.8197	0.6537	0.106*	
H14B	0.3898	0.7975	0.6951	0.106*	
H14C	0.4165	0.9078	0.6727	0.106*	
C15	0.25143 (19)	0.8715 (2)	0.57308 (17)	0.0878 (8)	
H15A	0.2587	0.9419	0.5846	0.132*	
H15B	0.2153	0.8401	0.6136	0.132*	
H15C	0.2114	0.8620	0.5195	0.132*	
O1	0.6121 (16)	0.7010 (16)	0.2444 (11)	0.0418 (18)	0.5

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0322 (2)	0.0701 (4)	0.0622 (3)	−0.0032 (2)	0.0121 (2)	−0.0040 (3)
N1	0.035 (3)	0.051 (3)	0.043 (5)	0.0008 (19)	0.017 (2)	−0.002 (3)
O2	0.0366 (7)	0.1019 (12)	0.0833 (10)	0.0177 (7)	0.0120 (7)	−0.0060 (9)
O3	0.0528 (8)	0.0783 (10)	0.0848 (10)	−0.0260 (7)	0.0188 (7)	−0.0017 (8)
N2	0.0564 (10)	0.0708 (12)	0.0595 (10)	0.0057 (8)	0.0213 (8)	−0.0053 (8)
C11	0.0430 (9)	0.0499 (10)	0.0401 (9)	−0.0004 (8)	0.0161 (8)	0.0007 (8)
C5	0.0422 (9)	0.0435 (10)	0.0411 (9)	0.0018 (7)	0.0023 (7)	−0.0002 (7)
C6	0.0387 (9)	0.0416 (9)	0.0426 (9)	−0.0021 (7)	0.0023 (7)	−0.0026 (7)
C1	0.0367 (9)	0.0517 (10)	0.0454 (10)	0.0024 (8)	0.0017 (7)	−0.0020 (8)
C10	0.0474 (10)	0.0508 (11)	0.0509 (11)	0.0029 (8)	0.0088 (8)	−0.0037 (8)
C12	0.0515 (11)	0.0591 (13)	0.0566 (11)	0.0084 (9)	0.0225 (9)	0.0023 (9)
C7	0.0572 (11)	0.0458 (10)	0.0478 (10)	0.0015 (9)	0.0101 (9)	0.0054 (8)
C4	0.0616 (12)	0.0523 (11)	0.0459 (10)	0.0048 (9)	0.0098 (9)	0.0076 (9)
C2	0.0543 (11)	0.0605 (12)	0.0585 (12)	0.0223 (9)	0.0033 (9)	0.0026 (10)
C9	0.0606 (12)	0.0543 (12)	0.0702 (13)	0.0212 (10)	0.0144 (10)	0.0039 (10)

C8	0.0715 (14)	0.0484 (11)	0.0626 (12)	0.0162 (10)	0.0074 (10)	0.0128 (9)
C13	0.0791 (14)	0.0509 (12)	0.0752 (14)	0.0108 (10)	0.0306 (13)	0.0021 (11)
C3	0.0775 (14)	0.0554 (12)	0.0570 (12)	0.0212 (11)	0.0078 (11)	0.0144 (10)
C14	0.0904 (17)	0.0706 (15)	0.0549 (13)	0.0006 (12)	0.0233 (12)	−0.0004 (11)
C15	0.0640 (14)	0.111 (2)	0.0949 (19)	0.0165 (14)	0.0343 (14)	−0.0055 (15)
O1	0.035 (3)	0.051 (3)	0.043 (5)	0.0008 (19)	0.017 (2)	−0.002 (3)

Geometric parameters (Å, º)

S1—N1	1.58 (3)	C12—H12	0.9300
S1—O2	1.4248 (14)	C12—C13	1.370 (3)
S1—O3	1.4189 (15)	C7—H7	0.9300
S1—C1	1.7681 (18)	C7—C8	1.354 (3)
S1—O1	1.67 (2)	C4—H4	0.9300
N1—H1	0.8600	C4—C3	1.348 (3)
N1—C11	1.44 (3)	C2—H2	0.9300
N2—C10	1.409 (2)	C2—C3	1.393 (3)
N2—C14	1.454 (3)	C9—H9	0.9300
N2—C15	1.459 (3)	C9—C8	1.389 (3)
C11—C11ⁱ	1.391 (3)	C8—H8	0.9300
C11—C12	1.377 (2)	C13—C13ⁱ	1.372 (4)
C11—O1	1.41 (2)	C13—H13	0.9300
C5—C6	1.429 (2)	C3—H3	0.9300
C5—C10	1.435 (2)	C14—H14A	0.9600
C5—C4	1.413 (2)	C14—H14B	0.9600
C6—C1	1.425 (2)	C14—H14C	0.9600
C6—C7	1.413 (2)	C15—H15A	0.9600
C1—C2	1.367 (3)	C15—H15B	0.9600
C10—C9	1.368 (3)	C15—H15C	0.9600
N1—S1—C1	98.6 (8)	C6—C7—H7	120.1
O2—S1—N1	112.1 (9)	C8—C7—C6	119.74 (17)
O2—S1—C1	108.28 (9)	C8—C7—H7	120.1
O2—S1—O1	105.4 (6)	C5—C4—H4	119.0
O3—S1—N1	104.3 (10)	C3—C4—C5	121.93 (18)
O3—S1—O2	119.29 (9)	C3—C4—H4	119.0
O3—S1—C1	112.27 (9)	C1—C2—H2	120.0
O3—S1—O1	104.0 (7)	C1—C2—C3	120.02 (18)
O1—S1—C1	106.6 (6)	C3—C2—H2	120.0
S1—N1—H1	118.6	C10—C9—H9	119.4
C11—N1—S1	122.8 (18)	C10—C9—C8	121.27 (18)
C11—N1—H1	118.6	C8—C9—H9	119.4
C10—N2—C14	116.97 (16)	C7—C8—C9	122.05 (18)
C10—N2—C15	116.09 (18)	C7—C8—H8	119.0
C14—N2—C15	110.84 (18)	C9—C8—H8	119.0
C11ⁱ—C11—N1	115.0 (10)	C12—C13—C13ⁱ	120.37 (12)
C11ⁱ—C11—O1	121.9 (8)	C12—C13—H13	119.8
C12—C11—N1	125.1 (10)	C13ⁱ—C13—H13	119.8

C12—C11—C11ⁱ	119.76 (11)	C4—C3—C2	120.24 (18)
C12—C11—O1	118.1 (8)	C4—C3—H3	119.9
C6—C5—C10	119.56 (15)	C2—C3—H3	119.9
C4—C5—C6	118.90 (16)	N2—C14—H14A	109.5
C4—C5—C10	121.37 (17)	N2—C14—H14B	109.5
C1—C6—C5	116.78 (15)	N2—C14—H14C	109.5
C7—C6—C5	118.75 (16)	H14A—C14—H14B	109.5
C7—C6—C1	124.40 (16)	H14A—C14—H14C	109.5
C6—C1—S1	121.67 (13)	H14B—C14—H14C	109.5
C2—C1—S1	116.02 (14)	N2—C15—H15A	109.5
C2—C1—C6	122.00 (17)	N2—C15—H15B	109.5
N2—C10—C5	118.17 (16)	N2—C15—H15C	109.5
C9—C10—N2	123.36 (17)	H15A—C15—H15B	109.5
C9—C10—C5	118.38 (17)	H15A—C15—H15C	109.5
C11—C12—H12	120.1	H15B—C15—H15C	109.5
C13—C12—C11	119.85 (18)	C11—O1—S1	117.7 (13)
C13—C12—H12	120.1		
S1—N1—C11—C11ⁱ	124.2 (13)	C6—C5—C4—C3	3.7 (3)
S1—N1—C11—C12	−51.6 (18)	C6—C1—C2—C3	1.1 (3)
S1—C1—C2—C3	−172.60 (16)	C6—C7—C8—C9	3.7 (3)
N1—S1—C1—C6	−67.6 (10)	C1—S1—N1—C11	−66.4 (15)
N1—S1—C1—C2	106.1 (10)	C1—S1—O1—C11	−48.7 (12)
N1—C11—C12—C13	174.6 (11)	C1—C6—C7—C8	174.71 (18)
O2—S1—N1—C11	47.5 (16)	C1—C2—C3—C4	−1.5 (3)
O2—S1—C1—C6	175.57 (14)	C10—C5—C6—C1	−179.37 (15)
O2—S1—C1—C2	−10.74 (18)	C10—C5—C6—C7	−2.3 (3)
O2—S1—O1—C11	66.2 (11)	C10—C5—C4—C3	179.07 (19)
O3—S1—N1—C11	177.9 (12)	C10—C9—C8—C7	−0.5 (3)
O3—S1—C1—C6	41.79 (17)	C12—C11—O1—S1	−72.7 (11)
O3—S1—C1—C2	−144.52 (15)	C7—C6—C1—S1	−2.0 (2)
O3—S1—O1—C11	−167.5 (9)	C7—C6—C1—C2	−175.27 (19)
N2—C10—C9—C8	179.6 (2)	C4—C5—C6—C1	−4.0 (2)
C11ⁱ—C11—C12—C13	−1.0 (3)	C4—C5—C6—C7	173.16 (17)
C11ⁱ—C11—O1—S1	112.6 (11)	C4—C5—C10—N2	6.6 (3)
C11—C12—C13—C13ⁱ	−0.6 (4)	C4—C5—C10—C9	−170.03 (19)
C5—C6—C1—S1	174.98 (12)	C14—N2—C10—C5	66.8 (2)
C5—C6—C1—C2	1.7 (3)	C14—N2—C10—C9	−116.8 (2)
C5—C6—C7—C8	−2.2 (3)	C15—N2—C10—C5	−159.33 (19)
C5—C10—C9—C8	−4.0 (3)	C15—N2—C10—C9	17.1 (3)
C5—C4—C3—C2	−1.0 (3)	O1—S1—C1—C6	−71.5 (8)
C6—C5—C10—N2	−178.08 (16)	O1—S1—C1—C2	102.2 (8)
C6—C5—C10—C9	5.3 (3)	O1—C11—C12—C13	−175.8 (9)

Symmetry code: (i) −*x*+1, *y*, −*z*+1/2.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C7—H7···O3	0.93	2.37	3.030 (2)	128
C13—H13···O3[ii]	0.93	2.73	3.386 (2)	129

Symmetry code: (ii) −*x*+3/2, *y*−1/2, −*z*+1/2.