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(4*Z*)-1-Methyl-4-[(2*E*)-2-(4-methylbenzylidene)hydrazin-1-ylidene]-3,4-dihydro-1*H*-2λ^6,1-benzothiazine-2,2-dione

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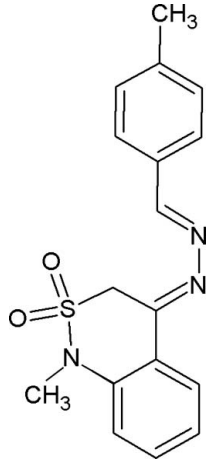
Key indicators: single-crystal X-ray study; T = 296 K; mean σ(C–C) = 0.013 Å; R factor = 0.120; wR factor = 0.347; data-to-parameter ratio = 13.4.

In the title compound, $C_{17}H_{17}N_3O_2S$, the dihedral angle between the aromatic rings is 6.3 (5)° and the C=N—N=C group is statistically planar [torsion angle = 179.8 (8)°]. The conformation of the thiazine ring is an envelope, with the S atom displaced by 0.823 (9) Å from the mean plane of the other five atoms (r.m.s. deviation = 0.012 Å). In the crystal, C—H···O interactions link the molecules into $C(5)$ chains propagating along [101]. The chains are consolidated by weak aromatic π–π stacking between the benzene and toluene rings [centroid-to-centroid separation = 3.826 (5) Å and interplanar angle = 6.3 (4)°].

Related literature

For the synthesis and biological activity of the title compound and related materials, see: Shafiq, Zia-ur-Rehman *et al.* (2011). For related structures, see: Shafiq, Khan *et al.* (2011); Shafiq *et al.* (2012). For C—H···O interactions, see: Steiner (2006). For graph-set nomenclature, see: Bernstein *et al.* (1995).



Experimental

Crystal data

$C_{17}H_{17}N_3O_2S$
M_r = 327.40
Monoclinic, $P2_1/n$
a = 7.899 (1) Å
b = 25.061 (3) Å
c = 8.1743 (11) Å
β = 101.114 (9)°
V = 1587.8 (3) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.22 mm^{-1}
T = 296 K
0.45 × 0.21 × 0.09 mm

Data collection

Bruker APEXII CCD diffractometer
13483 measured reflections
2877 independent reflections
1897 reflections with $I > 2\sigma(I)$
R_{int} = 0.049

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.120
$wR(F^2)$ = 0.347
S = 1.15
2877 reflections
215 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 1.44 e Å^{-3}
$\Delta\rho_{min}$ = −0.46 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
C16—H16A···O2^{i}	0.96	2.59	3.468 (13)	153

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

Data collection: *APEX2* (Bruker, 2007); cell refinement: *SAINT* (Bruker, 2007); 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); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: ZJ2094).

References

Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
Bruker (2007). *APEX2*, *SAINT* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Shafiq, M., Harrison, W. T. A., Khan, I. U., Bukhari, I. H. & Bokhari, T. H. (2012). *Acta Cryst.* E**68**, o2643.
Shafiq, M., Khan, I. U., Zia-ur-Rehman, M., Arshad, M. N. & Asiri, A. M. (2011). *Acta Cryst.* E**67**, o2092.
Shafiq, M., Zia-ur-Rehman, M., Khan, I. U., Arshad, M. N. & Khan, S. A. (2011). *J. Chil. Chem. Soc.* **56**, 527–531.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Steiner, Th. (2006). *Crystallogr. Rev.* 6, 1–57.

supporting information

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(4*Z*)-1-Methyl-4-[(2*E*)-2-(4-methylbenzylidene)hydrazin-1-ylidene]-3,4-dihydro-1*H*-2λ^6,1-benzothiazine-2,2-dione

Muhammad Shafiq, William T. A. Harrison, Islam Ullah Khan and Ejaz

S1. Comment

As part of our ongoing studies of benzothiazine derivatives with potential biological activity (Shafiq, Zia-ur-Rehman *et al.*, 2011), we now describe the crystal structure of the title compound, (I), (Fig. 1).

The dihedral angle between the aromatic rings (C1–C6 and C10–C15) in (I) is 6.3 (5)° and the C7═N2—N3═C9 torsion angle is 179.8 (8)°. Similar values have been seen in related structures (Shafiq, Khan *et al.*, 2011; Shafiq *et al.*, 2012). The conformation of the thiazine ring in (I) is an envelope, with the S atom displaced by 0.823 (9) Å from the mean plane of the other five atoms (r.m.s. deviation = 0.012 Å). Again, this is similar to the situation in related structures (Shafiq, Khan *et al.*, 2011; Shafiq *et al.*, 2012).

In the crystal of (I) (Fig. 2), weak C—H···O interactions (Steiner, 2006) (Table 1) link the molecules to generate C(5) chains propagating in [101]. The chains are consolidated by weak aromatic π–π stacking between the benzene and toluene rings [centroid-centroid separation = 3.826 (5) Å, inter-planar angle = 6.3 (4)°].

S2. Experimental

For the synthesis, see: Shafiq, Zia-ur-Rehman *et al.* (2011). Yellow blades were recrystallized from ethyl acetate. The crystal quality was poor, which may correlate with the rather high residuals.

S3. Refinement

The H atoms were placed in calculated positions (C—H = 0.93–0.97 Å) and refined as riding. The methyl group was allowed to rotate, but not to tip, to best fit the electron density. The constraint U_{iso}(H) = 1.2U_{eq}(C) or 1.5U_{eq}(methyl C) was applied. The highest difference peak is 1.27 Å from atom O2.

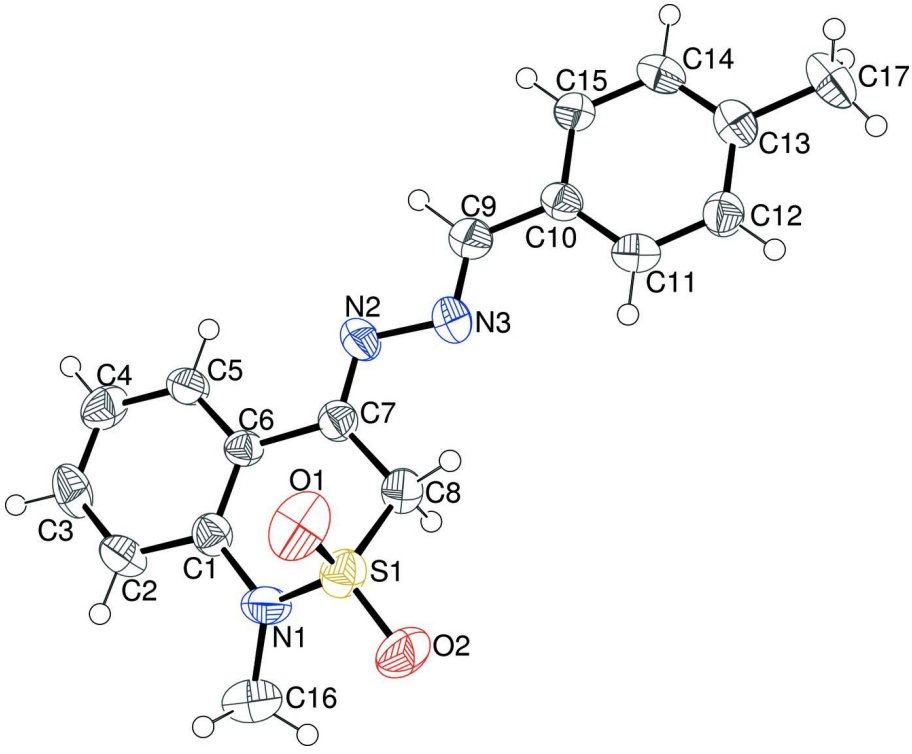

Figure 1

The molecular structure of (I), showing displacement ellipsoids at the 50% probability level.

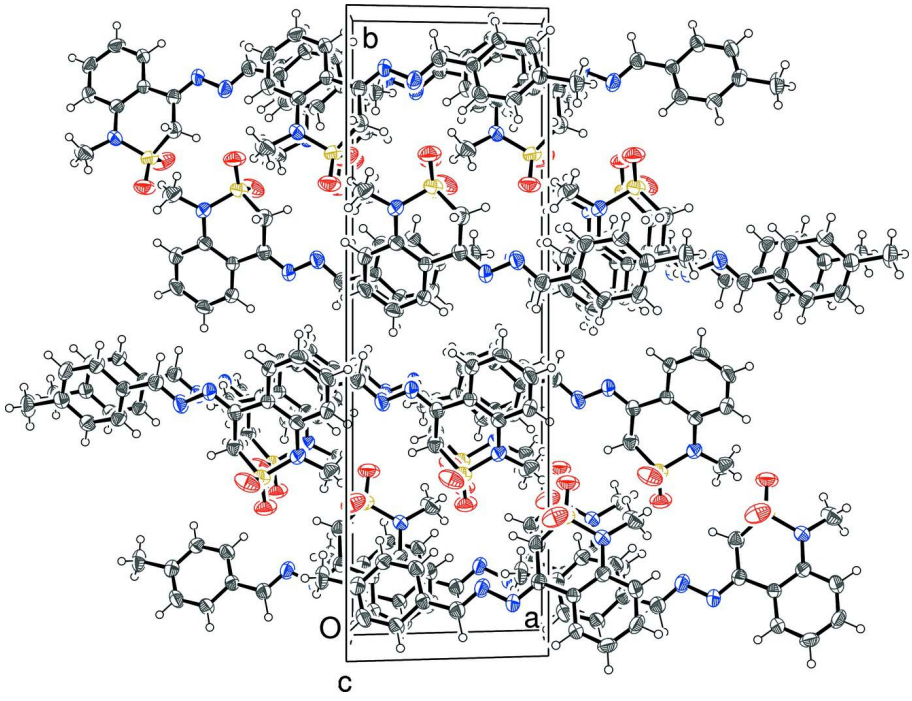

Figure 2

Detail of the packing of (I) showing part of a [101] chain of molecules linked by C—H···O hydrogen bonds (double dashed lines) and consolidated by aromatic π–π stacking between the centroids of the benzene and toluene rings (open pink lines). Symmetry codes: (i) -1/2 + x, 3/2 - y, -1/2 + z; (ii) -1 + x, y, -1 + z.

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Crystal data

$C_{17}H_{17}N_3O_2S$
M_r = 327.40
Monoclinic, $P2_1/n$
Hall symbol: -P 2yn
a = 7.899 (1) Å
b = 25.061 (3) Å
c = 8.1743 (11) Å
β = 101.114 (9)°
V = 1587.8 (3) Å^3
Z = 4
$F(000)$ = 688
D_x = 1.370 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 3678 reflections
θ = 2.8–24.9°
μ = 0.22 mm^{-1}
T = 296 K
Blade, yellow
0.45 × 0.21 × 0.09 mm

Data collection

Bruker APEXII CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
ω scans
13483 measured reflections
2877 independent reflections
1897 reflections with $I > 2\sigma(I)$
R_{int} = 0.049
θ_{max} = 25.3°, θ_{min} = 2.7°
h = −9→9
k = −30→30
l = −9→9

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.120$
$wR(F^2) = 0.347$
$S = 1.15$
2877 reflections
215 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0894P)^2 + 15.6763P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 1.44$ e Å^{-3}
$\Delta\rho_{min} = -0.46$ e Å^{-3}
Extinction correction: *SHELXL97* (Sheldrick, 2008), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.011 (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 (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.2464 (11)	0.6374 (3)	0.1249 (10)	0.0393 (19)
C2	0.0924 (11)	0.6173 (4)	0.0246 (12)	0.048 (2)
H2	−0.0062	0.6384	0.0023	0.058*
C3	0.0902 (12)	0.5668 (4)	−0.0386 (13)	0.052 (2)
H3	−0.0107	0.5539	−0.1047	0.063*
C4	0.2323 (12)	0.5349 (4)	−0.0072 (12)	0.050 (2)
H4	0.2283	0.5005	−0.0500	0.060*
C5	0.3802 (11)	0.5541 (3)	0.0875 (11)	0.042 (2)
H5	0.4779	0.5326	0.1070	0.050*
C6	0.3899 (10)	0.6050 (3)	0.1561 (10)	0.0329 (17)
C7	0.5555 (10)	0.6233 (3)	0.2611 (10)	0.0378 (19)
C8	0.5629 (11)	0.6777 (3)	0.3398 (11)	0.046 (2)
H8A	0.6805	0.6908	0.3583	0.055*
H8B	0.5283	0.6751	0.4471	0.055*
C9	0.9564 (11)	0.5776 (4)	0.4027 (12)	0.045 (2)
H9	0.928 (13)	0.538 (4)	0.348 (12)	0.07 (3)*
C10	1.1248 (10)	0.5891 (3)	0.5059 (10)	0.0362 (19)
C11	1.1580 (11)	0.6354 (4)	0.5998 (11)	0.045 (2)
H11	1.0710	0.6606	0.5980	0.054*
C12	1.3211 (11)	0.6445 (3)	0.6965 (11)	0.044 (2)
H12	1.3421	0.6755	0.7598	0.053*
C13	1.4514 (11)	0.6077 (4)	0.6988 (11)	0.043 (2)
C14	1.4177 (11)	0.5616 (4)	0.6071 (12)	0.051 (2)

H14	1.5050	0.5365	0.6101	0.062*
C15	1.2550 (10)	0.5515 (4)	0.5095 (10)	0.041 (2)
H15	1.2343	0.5202	0.4480	0.049*
C16	0.0902 (13)	0.7157 (4)	0.2205 (13)	0.059 (3)
H16A	0.0280	0.7308	0.1185	0.089*
H16B	0.1207	0.7435	0.3017	0.089*
H16C	0.0189	0.6899	0.2617	0.089*
C17	1.6295 (12)	0.6184 (5)	0.8015 (14)	0.064 (3)
H17A	1.7116	0.6205	0.7292	0.096*
H17B	1.6610	0.5900	0.8802	0.096*
H17C	1.6284	0.6516	0.8602	0.096*
S1	0.4268 (3)	0.72269 (9)	0.2121 (3)	0.0472 (7)
N1	0.2450 (9)	0.6901 (3)	0.1900 (11)	0.052 (2)
N2	0.6832 (9)	0.5911 (3)	0.2813 (9)	0.0448 (18)
N3	0.8324 (9)	0.6113 (3)	0.3859 (10)	0.0477 (19)
O1	0.4836 (11)	0.7265 (3)	0.0588 (9)	0.069 (2)
O2	0.4100 (10)	0.7710 (2)	0.3007 (9)	0.064 (2)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.038 (5)	0.036 (4)	0.042 (5)	−0.003 (4)	0.004 (4)	0.001 (4)
C2	0.033 (5)	0.049 (5)	0.061 (6)	0.006 (4)	0.004 (4)	0.006 (4)
C3	0.038 (5)	0.050 (6)	0.062 (6)	−0.016 (4)	−0.009 (4)	0.003 (5)
C4	0.057 (6)	0.033 (5)	0.061 (6)	−0.008 (4)	0.016 (5)	−0.011 (4)
C5	0.032 (4)	0.039 (5)	0.054 (5)	0.004 (4)	0.006 (4)	−0.004 (4)
C6	0.031 (4)	0.032 (4)	0.037 (4)	0.000 (3)	0.009 (3)	0.000 (3)
C7	0.036 (4)	0.042 (5)	0.036 (5)	−0.001 (4)	0.007 (4)	−0.001 (4)
C8	0.042 (5)	0.051 (5)	0.043 (5)	−0.001 (4)	0.006 (4)	−0.006 (4)
C9	0.039 (5)	0.047 (5)	0.048 (5)	0.001 (4)	0.010 (4)	−0.004 (4)
C10	0.034 (4)	0.040 (4)	0.035 (4)	0.004 (3)	0.008 (4)	0.006 (3)
C11	0.042 (5)	0.045 (5)	0.051 (5)	0.007 (4)	0.015 (4)	0.000 (4)
C12	0.043 (5)	0.041 (5)	0.046 (5)	−0.003 (4)	0.004 (4)	−0.004 (4)
C13	0.038 (5)	0.050 (5)	0.040 (5)	−0.003 (4)	0.005 (4)	0.011 (4)
C14	0.036 (5)	0.055 (6)	0.062 (6)	0.013 (4)	0.006 (4)	0.000 (5)
C15	0.038 (5)	0.045 (5)	0.040 (5)	0.006 (4)	0.006 (4)	−0.004 (4)
C16	0.067 (7)	0.051 (6)	0.066 (7)	0.013 (5)	0.028 (5)	0.005 (5)
C17	0.034 (5)	0.086 (8)	0.065 (7)	−0.001 (5)	−0.004 (5)	0.013 (6)
S1	0.0551 (15)	0.0354 (12)	0.0503 (14)	−0.0034 (10)	0.0081 (11)	−0.0015 (10)
N1	0.038 (4)	0.040 (4)	0.078 (6)	0.005 (3)	0.010 (4)	−0.012 (4)
N2	0.030 (4)	0.048 (4)	0.053 (5)	−0.001 (3)	0.001 (3)	−0.004 (3)
N3	0.035 (4)	0.054 (5)	0.052 (5)	−0.006 (3)	0.002 (3)	−0.007 (4)
O1	0.099 (6)	0.059 (4)	0.057 (4)	−0.025 (4)	0.033 (4)	0.004 (3)
O2	0.081 (5)	0.037 (3)	0.073 (5)	0.004 (3)	0.010 (4)	−0.013 (3)

Geometric parameters (Å, º)

C1—C6	1.378 (11)	C10—C15	1.391 (11)
C1—C2	1.421 (12)	C11—C12	1.394 (12)
C1—N1	1.424 (11)	C11—H11	0.9300
C2—C3	1.366 (13)	C12—C13	1.378 (12)
C2—H2	0.9300	C12—H12	0.9300
C3—C4	1.362 (13)	C13—C14	1.377 (13)
C3—H3	0.9300	C13—C17	1.517 (12)
C4—C5	1.359 (12)	C14—C15	1.398 (12)
C4—H4	0.9300	C14—H14	0.9300
C5—C6	1.388 (11)	C15—H15	0.9300
C5—H5	0.9300	C16—N1	1.445 (11)
C6—C7	1.493 (11)	C16—H16A	0.9600
C7—N2	1.278 (10)	C16—H16B	0.9600
C7—C8	1.502 (12)	C16—H16C	0.9600
C8—S1	1.757 (9)	C17—H17A	0.9600
C8—H8A	0.9700	C17—H17B	0.9600
C8—H8B	0.9700	C17—H17C	0.9600
C9—N3	1.280 (11)	S1—O1	1.414 (7)
C9—C10	1.459 (12)	S1—O2	1.430 (6)
C9—H9	1.10 (10)	S1—N1	1.632 (8)
C10—C11	1.390 (12)	N2—N3	1.410 (9)
C6—C1—C2	118.7 (7)	C13—C12—C11	120.3 (8)
C6—C1—N1	122.8 (7)	C13—C12—H12	119.8
C2—C1—N1	118.4 (7)	C11—C12—H12	119.8
C3—C2—C1	119.5 (8)	C14—C13—C12	119.3 (8)
C3—C2—H2	120.2	C14—C13—C17	120.8 (9)
C1—C2—H2	120.2	C12—C13—C17	120.0 (9)
C4—C3—C2	121.5 (8)	C13—C14—C15	121.5 (8)
C4—C3—H3	119.2	C13—C14—H14	119.3
C2—C3—H3	119.2	C15—C14—H14	119.3
C5—C4—C3	119.1 (8)	C10—C15—C14	119.0 (8)
C5—C4—H4	120.4	C10—C15—H15	120.5
C3—C4—H4	120.4	C14—C15—H15	120.5
C4—C5—C6	122.0 (8)	N1—C16—H16A	109.5
C4—C5—H5	119.0	N1—C16—H16B	109.5
C6—C5—H5	119.0	H16A—C16—H16B	109.5
C1—C6—C5	119.2 (7)	N1—C16—H16C	109.5
C1—C6—C7	121.6 (7)	H16A—C16—H16C	109.5
C5—C6—C7	119.3 (7)	H16B—C16—H16C	109.5
N2—C7—C6	117.5 (7)	C13—C17—H17A	109.5
N2—C7—C8	123.6 (8)	C13—C17—H17B	109.5
C6—C7—C8	118.9 (7)	H17A—C17—H17B	109.5
C7—C8—S1	111.0 (6)	C13—C17—H17C	109.5
C7—C8—H8A	109.4	H17A—C17—H17C	109.5
S1—C8—H8A	109.4	H17B—C17—H17C	109.5

C7—C8—H8B	109.4	O1—S1—O2	117.9 (4)
S1—C8—H8B	109.4	O1—S1—N1	111.0 (5)
H8A—C8—H8B	108.0	O2—S1—N1	108.3 (4)
N3—C9—C10	121.7 (8)	O1—S1—C8	107.9 (5)
N3—C9—H9	118 (5)	O2—S1—C8	110.4 (4)
C10—C9—H9	120 (5)	N1—S1—C8	99.7 (4)
C11—C10—C15	119.6 (8)	C1—N1—C16	123.0 (8)
C11—C10—C9	122.5 (8)	C1—N1—S1	115.8 (6)
C15—C10—C9	117.9 (8)	C16—N1—S1	120.9 (6)
C10—C11—C12	120.3 (8)	C7—N2—N3	113.4 (7)
C10—C11—H11	119.8	C9—N3—N2	111.1 (7)
C12—C11—H11	119.8		

C6—C1—C2—C3	−0.3 (13)	C11—C12—C13—C17	178.7 (8)
N1—C1—C2—C3	−179.7 (9)	C12—C13—C14—C15	1.1 (14)
C1—C2—C3—C4	0.4 (15)	C17—C13—C14—C15	−178.9 (9)
C2—C3—C4—C5	−0.9 (15)	C11—C10—C15—C14	−0.5 (12)
C3—C4—C5—C6	1.3 (14)	C9—C10—C15—C14	179.8 (8)
C2—C1—C6—C5	0.7 (12)	C13—C14—C15—C10	−0.2 (14)
N1—C1—C6—C5	−179.9 (8)	C7—C8—S1—O1	−60.6 (7)
C2—C1—C6—C7	−179.6 (8)	C7—C8—S1—O2	169.2 (6)
N1—C1—C6—C7	−0.3 (12)	C7—C8—S1—N1	55.4 (7)
C4—C5—C6—C1	−1.2 (13)	C6—C1—N1—C16	−153.1 (9)
C4—C5—C6—C7	179.1 (8)	C2—C1—N1—C16	26.3 (13)
C1—C6—C7—N2	−178.7 (8)	C6—C1—N1—S1	32.7 (11)
C5—C6—C7—N2	0.9 (11)	C2—C1—N1—S1	−147.9 (7)
C1—C6—C7—C8	2.5 (11)	O1—S1—N1—C1	57.5 (8)
C5—C6—C7—C8	−177.9 (8)	O2—S1—N1—C1	−171.6 (6)
N2—C7—C8—S1	148.3 (7)	C8—S1—N1—C1	−56.1 (7)
C6—C7—C8—S1	−33.0 (9)	O1—S1—N1—C16	−116.9 (8)
N3—C9—C10—C11	4.0 (13)	O2—S1—N1—C16	14.1 (9)
N3—C9—C10—C15	−176.4 (8)	C8—S1—N1—C16	129.5 (8)
C15—C10—C11—C12	0.3 (13)	C6—C7—N2—N3	−178.3 (7)
C9—C10—C11—C12	179.9 (8)	C8—C7—N2—N3	0.4 (12)
C10—C11—C12—C13	0.6 (13)	C10—C9—N3—N2	−179.7 (7)
C11—C12—C13—C14	−1.3 (13)	C7—N2—N3—C9	179.8 (8)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C16—H16*A*···O2^{i}	0.96	2.59	3.468 (13)	153

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