

Crystal structure of 2-(2,4-dichlorophenyl)-4-hydroxy-9-phenylsulfonyl-9*H*-carbazole-3-carbaldehyde

M. Umadevi,^{a,b} B. M. Ramalingam,^c R. Yamuna,^{d*} A. K. Mohanakrishnan^c and G. Chakkaravarthi^{e,*}

Received 18 October 2014

Accepted 31 October 2014

Edited by V. V. Chernyshev, Moscow State University, Russia

^aResearch and Development Centre, Bharathiyar University, India, ^bDepartment of Chemistry, Pallavan College of Engineering, Kanchipuram, Tamilnadu, India, ^cDepartment of Organic Chemistry, University of Madras, Guindy Campus, Chennai 600 025, India, ^dDepartment of Sciences, Chemistry and Materials Research Laboratory, Amrita Vishwa Vidyapeetham University, Ettimadai, Coimbatore 641 112, India, and ^eDepartment of Physics, CPCL Polytechnic College, Chennai

600 068, India. *Correspondence e-mail: ryamuna1@gmail.com, chakkaravarthi_2005@yahoo.com

Keywords: crystal structure; carbazole derivative; hydrogen bonding

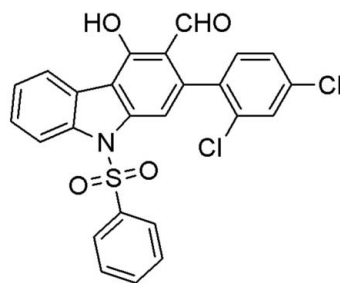
CCDC reference: 1032055

Supporting information: this article has supporting information at journals.iucr.org/e

In the title compound, C₂₅H₁₅Cl₂NO₄S, the dichlorophenyl ring is twisted by 68.69 (11)° from the mean plane of the carbazole ring system [r.m.s. deviation = 0.084 (2)°]. The hydroxy group is involved in an intramolecular O—H···O hydrogen bond, which generates an *S*(6) graph-set motif. In the crystal, pairs of C—H···Cl hydrogen bonds link molecules into inversion dimers with an *R*₂²(26) motif. Weak C—H···O interactions further link these dimers into ribbons propagating in [100].

1. Chemical context

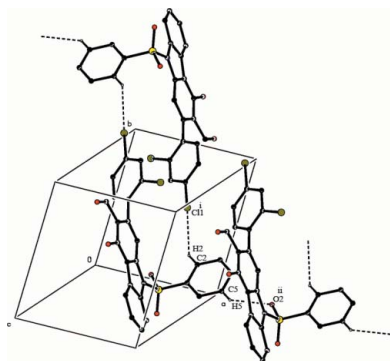
In continuation of our studies of carbazole derivatives, which are found to possess various biological activities, such as anti-oxidative (Tachibana *et al.*, 2001), anti-inflammatory and antimutagenic (Ramsewak *et al.*, 1999), antibiotic, antifungal and cytotoxic (Chakraborty *et al.*, 1965, 1978), we report herein on the synthesis and crystal structure of the title compound (I) (Fig. 1).



2. Structural commentary

The geometric parameters of (I) agree well with those reported for related structures [Chakkaravarthi *et al.* 2008, 2009]. The C1–C6 phenyl ring makes a dihedral angle of 79.76 (11)° with the carbazole ring system (C7–C18/N1). The dichlorophenyl ring (C21–C25) is twisted by 68.69 (11)° from the mean plane of the carbazole ring system and inclined at an angle of 32.22 (13)° to the phenyl ring.

Atom S1 has a distorted tetrahedral configuration. The widening of angle O1–S1–O2 [120.49 (11)°] and narrowing of angle N1–S1–C1 [105.36 (10)°] from the ideal tetrahedral values are attributed to the Thorpe–Ingold effect (Bassindale, 1984). As a result of the electron-withdrawing character of the



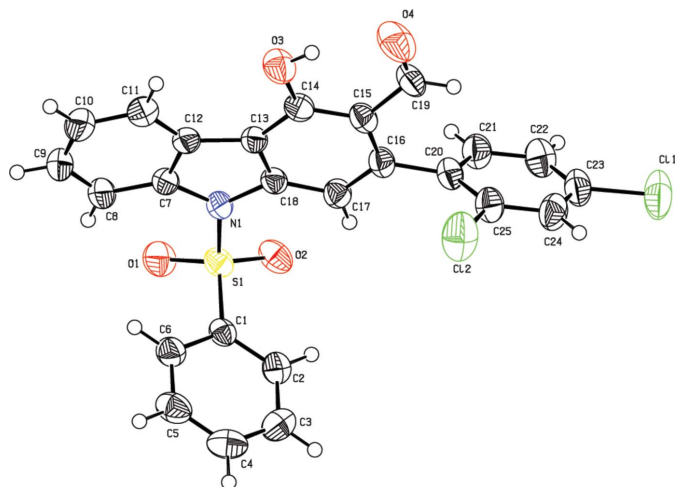


Figure 1
The molecular structure of (I) showing the atomic labelling scheme and 50% probability displacement ellipsoids.

phenylsulfonyl group, the bond lengths N1–C7 [1.431 (3) Å] and N1–C18 [1.414 (3) Å] in the molecule are longer than the mean value of 1.355 (14) Å (Allen *et al.*, 1987; Groom & Allen *et al.*, 2014).

3. Supramolecular features

The hydroxy group is involved in an intramolecular O–H···O hydrogen bond (Table 1), which generates an *S*(6) graph-set motif. In the crystal, pairs of C–H···Cl hydrogen bonds link molecules into inversion dimers with an *R*₂²(26) motif (Bernstein *et al.*, 1995), and weak C–H···O interactions further link these dimers into ribbons propagating in [100] (Table 1 and Fig. 2).

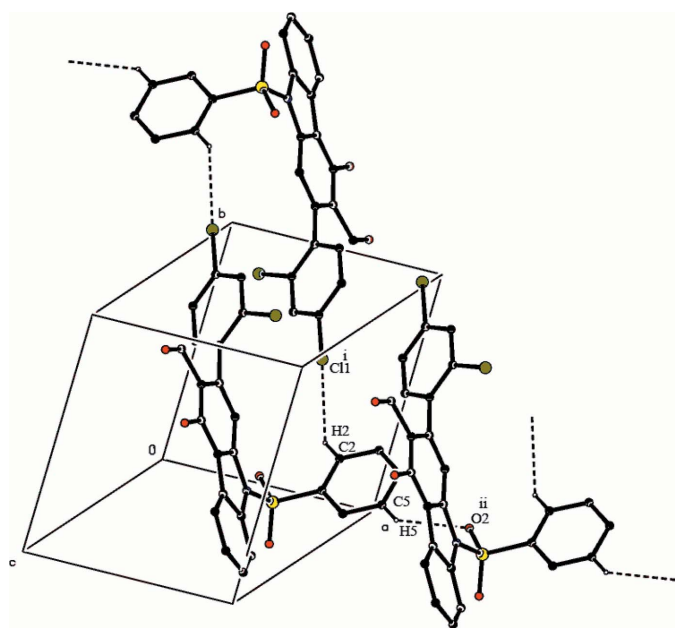


Figure 2
A portion of the crystal packing of (I) showing the hydrogen-bonded (dashed lines) ribbon [symmetry codes: (i) 1-*x*, 2-*y*, 1-*z*; (ii) 1 + *x*, *y*, *z*].

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

<i>D</i> –H··· <i>A</i>	<i>D</i> –H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> –H··· <i>A</i>
O3–H3A···O4	0.83 (1)	1.81 (2)	2.563 (3)	151 (3)
C2–H2···Cl1 ⁱ	0.93	2.81	3.412 (2)	123
C5–H5···O2 ⁱⁱ	0.93	2.49	3.184 (3)	131

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

4. Synthesis and crystallization

Enamine 16 g (500 mg, 0.95 mmol) was reacted with CuBr₂ (212 mg, 0.95 mmol) in dry DMF (20 ml) at reflux for 1 h under N₂. The reaction mass was poured over crushed ice (50 ml) containing concentrated HCl (1 ml). The precipitated solid was filtered, washed with water and air-dried to obtain the crude compound, which was purified by flash column chromatography on silica gel (230–420 mesh, *n*-hexane/ethyl acetate, 7:3) to afford 17 g as pale-yellow crystals suitable for X-ray analysis. Yield: 368 mg (78%); m.p.: 461–463 K.

5. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The hydroxy H atom was located in a difference Fourier map and refined isotropically with a distance restraint of O–H = 0.82 (1) Å. All other H atoms

Table 2
Experimental details.

Crystal data	
Chemical formula	C ₂₅ H ₁₅ Cl ₂ NO ₄ S
<i>M_r</i>	496.34
Crystal system, space group	Triclinic, <i>P</i> $\bar{1}$
Temperature (K)	295
<i>a</i> , <i>b</i> , <i>c</i> (Å)	8.0688 (4), 9.9086 (5), 14.4041 (8)
α , β , γ (°)	75.297 (3), 80.604 (2), 74.306 (3)
<i>V</i> (Å ³)	1066.83 (10)
<i>Z</i>	2
Radiation type	Mo <i>K</i> α
μ (mm ⁻¹)	0.44
Crystal size (mm)	0.28 × 0.24 × 0.18
Data collection	
Diffractometer	Bruker Kappa APEXII CCD
Absorption correction	Multi-scan (<i>SADABS</i> ; Sheldrick, 1996)
<i>T_{min}</i> , <i>T_{max}</i>	0.887, 0.925
No. of measured, independent and observed [<i>I</i> > 2 σ (<i>I</i>)] reflections	35959, 6221, 3582
<i>R_{int}</i>	0.044
(<i>sin</i> θ / λ) _{max} (Å ⁻¹)	0.735
Refinement	
<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.048, 0.126, 1.02
No. of reflections	6221
No. of parameters	302
No. of restraints	2
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å ⁻³)	0.44, -0.48

Computer programs: *APEX2* and *SAINT* (Bruker, 2004), *SHELXS97* and *SHELXL97* (Sheldrick, 2008) and *PLATON* (Spek, 2009).

were positioned geometrically and refined using a riding model, with C—H = 0.93 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. The components of the anisotropic displacement parameters in the direction of the bond between O4 and C19 were restrained to be equal within an effective standard deviation of 0.001 using the DELU command in *SHELXL97* (Sheldrick, 2008).

Acknowledgements

The authors acknowledge the SAIF, IIT, Madras for the data collection.

References

- Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin. Trans. 2*, pp. S1–19.
- Bassindale, A. (1984). *The Third Dimension in Organic Chemistry*, ch. 1, p. 11. New York: John Wiley and Sons.
- Bernstein, J., Davis, R. E., Shimon, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
- Bruker (2004). *APEX2* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Chakkaravarthi, G., Dhayalan, V., Mohanakrishnan, A. K. & Manivannan, V. (2008). *Acta Cryst.* **E64**, o1667–o1668.
- Chakkaravarthi, G., Marx, A., Dhayalan, V., Mohanakrishnan, A. K. & Manivannan, V. (2009). *Acta Cryst.* **E65**, o464–o465.
- Chakraborty, D. P., Barman, B. K. & Bose, P. K. (1965). *Tetrahedron*, **21**, 681–685.
- Chakraborty, D. P., Bhattacharyya, P., Roy, S., Bhattacharyya, S. P. & Biswas, A. K. (1978). *Phytochemistry*, **17**, 834–835.
- Groom, C. R. & Allen, F. H. (2014). *Angew. Chem. Int. Ed.* **53**, 662–671.
- Ramsewak, R. S., Nair, M. G., Strasburg, G. M., DeWitt, D. L. & Nitiss, J. L. (1999). *J. Agric. Food Chem.* **47**, 444–447.
- Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Spek, A. L. (2009). *Acta Cryst.* **D65**, 148–155.
- Tachibana, Y., Kikuzaki, H., Lajis, N. H. & Nakatani, N. (2001). *J. Agric. Food Chem.* **49**, 5589–5594.

supporting information

Acta Cryst. (2014). E70, 466–468 [doi:10.1107/S1600536814024064]

Crystal structure of 2-(2,4-dichlorophenyl)-4-hydroxy-9-phenylsulfonyl-9H-carbazole-3-carbaldehyde

M. Umadevi, B. M. Ramalingam, R. Yamuna, A. K. Mohanakrishnan and G. Chakkaravarthi

Computing details

Data collection: *APEX2* (Bruker, 2004); cell refinement: *SAINTE* (Bruker, 2004); data reduction: *SAINTE* (Bruker, 2004); 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* (Sheldrick, 2008).

2-(2,4-Dichlorophenyl)-4-hydroxy-9-phenylsulfonyl-9H-carbazole-3-carbaldehyde

Crystal data

$C_{25}H_{15}Cl_2NO_4S$
 $M_r = 496.34$
 Triclinic, $P\bar{1}$
 Hall symbol: -P 1
 $a = 8.0688$ (4) Å
 $b = 9.9086$ (5) Å
 $c = 14.4041$ (8) Å
 $\alpha = 75.297$ (3)°
 $\beta = 80.604$ (2)°
 $\gamma = 74.306$ (3)°
 $V = 1066.83$ (10) Å³

$Z = 2$
 $F(000) = 508$
 $D_x = 1.545$ Mg m⁻³
 Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
 Cell parameters from 9493 reflections
 $\theta = 2.2$ – 31.5 °
 $\mu = 0.44$ mm⁻¹
 $T = 295$ K
 Block, pale yellow
 $0.28 \times 0.24 \times 0.18$ mm

Data collection

Bruker Kappa APEXII CCD
 diffractometer
 Radiation source: fine-focus sealed tube
 Graphite monochromator
 ω and ϕ scan
 Absorption correction: multi-scan
 (*SADABS*; Sheldrick, 1996)
 $T_{\min} = 0.887$, $T_{\max} = 0.925$

35959 measured reflections
 6221 independent reflections
 3582 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.044$
 $\theta_{\max} = 31.5$ °, $\theta_{\min} = 2.2$ °
 $h = -11 \rightarrow 11$
 $k = -14 \rightarrow 13$
 $l = -19 \rightarrow 21$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.048$
 $wR(F^2) = 0.126$
 $S = 1.02$
 6221 reflections
 302 parameters
 2 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

$$w = 1/[\sigma^2(F_o^2) + (0.0395P)^2 + 0.6935P]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$

$$\Delta\rho_{\max} = 0.44 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.48 \text{ e } \text{\AA}^{-3}$$

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds 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 $F^2 > 2\text{sigma}(F^2)$ 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	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	1.0997 (3)	0.3850 (2)	0.70308 (15)	0.0345 (5)
C2	1.0940 (3)	0.4840 (3)	0.61674 (17)	0.0471 (6)
H2	0.9939	0.5159	0.5854	0.057*
C3	1.2388 (4)	0.5356 (3)	0.5769 (2)	0.0582 (7)
H3	1.2371	0.6018	0.5181	0.070*
C4	1.3848 (3)	0.4886 (3)	0.6244 (2)	0.0551 (7)
H4	1.4821	0.5234	0.5974	0.066*
C5	1.3893 (3)	0.3910 (3)	0.71103 (19)	0.0524 (6)
H5	1.4889	0.3607	0.7428	0.063*
C6	1.2472 (3)	0.3379 (3)	0.75090 (17)	0.0445 (5)
H6	1.2499	0.2710	0.8094	0.053*
C7	0.8949 (3)	0.3246 (2)	0.94145 (16)	0.0384 (5)
C8	1.0086 (3)	0.1961 (2)	0.97765 (19)	0.0483 (6)
H8	1.0604	0.1300	0.9395	0.058*
C9	1.0419 (3)	0.1703 (3)	1.07175 (19)	0.0530 (6)
H9	1.1187	0.0853	1.0975	0.064*
C10	0.9647 (3)	0.2669 (3)	1.12916 (19)	0.0557 (7)
H10	0.9915	0.2468	1.1924	0.067*
C11	0.8483 (3)	0.3927 (3)	1.09402 (17)	0.0487 (6)
H11	0.7938	0.4565	1.1334	0.058*
C12	0.8138 (3)	0.4224 (2)	0.99882 (16)	0.0376 (5)
C13	0.7085 (3)	0.5439 (2)	0.93908 (15)	0.0349 (5)
C14	0.5999 (3)	0.6708 (2)	0.95850 (16)	0.0387 (5)
C15	0.5169 (3)	0.7739 (2)	0.88353 (17)	0.0404 (5)
C16	0.5471 (3)	0.7497 (2)	0.78918 (17)	0.0391 (5)
C17	0.6519 (3)	0.6224 (2)	0.76991 (16)	0.0392 (5)
H17	0.6704	0.6054	0.7080	0.047*
C18	0.7289 (3)	0.5206 (2)	0.84630 (16)	0.0350 (5)
C19	0.3929 (3)	0.9054 (3)	0.9062 (2)	0.0491 (6)
H19	0.3362	0.9730	0.8567	0.059*
C20	0.4596 (3)	0.8596 (2)	0.70952 (17)	0.0415 (5)
C21	0.3271 (3)	0.8330 (3)	0.67214 (19)	0.0500 (6)

H21	0.2988	0.7447	0.6954	0.060*
C22	0.2357 (4)	0.9332 (3)	0.6016 (2)	0.0578 (7)
H22	0.1467	0.9132	0.5777	0.069*
C23	0.2786 (4)	1.0625 (3)	0.56730 (18)	0.0529 (6)
C24	0.4114 (4)	1.0926 (2)	0.60002 (19)	0.0534 (6)
H24	0.4407	1.1803	0.5752	0.064*
C25	0.5009 (3)	0.9905 (2)	0.67056 (18)	0.0478 (6)
N1	0.8388 (2)	0.38241 (18)	0.84706 (13)	0.0383 (4)
O1	0.9772 (2)	0.16411 (16)	0.78521 (13)	0.0539 (5)
O2	0.7943 (2)	0.37100 (18)	0.68385 (12)	0.0480 (4)
O3	0.5763 (2)	0.6893 (2)	1.04911 (13)	0.0545 (5)
O4	0.3634 (3)	0.9274 (2)	0.98621 (16)	0.0726 (6)
S1	0.92029 (7)	0.31431 (6)	0.75094 (4)	0.03877 (15)
Cl1	0.16251 (12)	1.19156 (9)	0.48058 (6)	0.0826 (3)
Cl2	0.66928 (11)	1.03092 (8)	0.71005 (7)	0.0781 (3)
H3A	0.512 (4)	0.7704 (18)	1.047 (2)	0.084 (11)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0343 (11)	0.0338 (10)	0.0355 (12)	-0.0022 (9)	-0.0034 (9)	-0.0143 (9)
C2	0.0419 (13)	0.0501 (14)	0.0455 (14)	-0.0059 (11)	-0.0096 (11)	-0.0059 (11)
C3	0.0609 (17)	0.0609 (16)	0.0473 (15)	-0.0190 (14)	-0.0006 (13)	-0.0007 (12)
C4	0.0466 (15)	0.0690 (17)	0.0585 (17)	-0.0252 (13)	0.0080 (12)	-0.0257 (14)
C5	0.0367 (13)	0.0736 (18)	0.0516 (16)	-0.0115 (12)	-0.0065 (11)	-0.0229 (13)
C6	0.0376 (12)	0.0531 (14)	0.0401 (13)	-0.0060 (11)	-0.0060 (10)	-0.0093 (11)
C7	0.0346 (11)	0.0329 (11)	0.0424 (13)	-0.0066 (9)	0.0005 (9)	-0.0035 (9)
C8	0.0454 (14)	0.0340 (12)	0.0541 (15)	-0.0009 (10)	0.0008 (11)	-0.0024 (11)
C9	0.0464 (14)	0.0433 (13)	0.0551 (16)	-0.0019 (11)	-0.0061 (12)	0.0055 (12)
C10	0.0512 (15)	0.0641 (17)	0.0435 (14)	-0.0102 (13)	-0.0095 (12)	0.0017 (13)
C11	0.0479 (14)	0.0527 (14)	0.0409 (14)	-0.0082 (11)	-0.0015 (11)	-0.0082 (11)
C12	0.0344 (11)	0.0346 (11)	0.0404 (12)	-0.0089 (9)	0.0014 (9)	-0.0047 (9)
C13	0.0333 (11)	0.0311 (10)	0.0380 (12)	-0.0068 (8)	-0.0012 (9)	-0.0058 (9)
C14	0.0378 (12)	0.0394 (12)	0.0401 (12)	-0.0083 (9)	-0.0018 (10)	-0.0134 (10)
C15	0.0358 (12)	0.0334 (11)	0.0503 (14)	-0.0030 (9)	-0.0047 (10)	-0.0119 (10)
C16	0.0381 (12)	0.0313 (11)	0.0454 (13)	-0.0041 (9)	-0.0075 (10)	-0.0066 (9)
C17	0.0416 (12)	0.0350 (11)	0.0392 (12)	-0.0055 (9)	-0.0039 (10)	-0.0091 (9)
C18	0.0320 (11)	0.0286 (10)	0.0418 (12)	-0.0059 (8)	0.0001 (9)	-0.0070 (9)
C19	0.0362 (12)	0.0467 (13)	0.0581 (13)	0.0058 (10)	-0.0078 (11)	-0.0156 (11)
C20	0.0405 (12)	0.0339 (11)	0.0467 (13)	-0.0007 (9)	-0.0088 (10)	-0.0090 (10)
C21	0.0489 (14)	0.0408 (13)	0.0574 (16)	-0.0077 (11)	-0.0114 (12)	-0.0052 (11)
C22	0.0556 (16)	0.0552 (16)	0.0614 (17)	-0.0051 (13)	-0.0195 (13)	-0.0109 (13)
C23	0.0593 (16)	0.0433 (14)	0.0470 (15)	0.0084 (12)	-0.0148 (12)	-0.0099 (11)
C24	0.0685 (18)	0.0326 (12)	0.0525 (15)	-0.0043 (12)	-0.0093 (13)	-0.0040 (11)
C25	0.0506 (14)	0.0362 (12)	0.0555 (15)	-0.0057 (11)	-0.0125 (12)	-0.0085 (11)
N1	0.0386 (10)	0.0305 (9)	0.0398 (10)	-0.0009 (8)	-0.0004 (8)	-0.0074 (8)
O1	0.0599 (11)	0.0312 (8)	0.0680 (12)	-0.0069 (8)	0.0004 (9)	-0.0150 (8)
O2	0.0350 (8)	0.0574 (10)	0.0583 (11)	-0.0074 (7)	-0.0119 (8)	-0.0239 (8)

O3	0.0574 (11)	0.0555 (11)	0.0474 (10)	0.0035 (9)	-0.0069 (8)	-0.0232 (9)
O4	0.0674 (13)	0.0700 (13)	0.0780 (12)	0.0113 (10)	-0.0090 (11)	-0.0405 (11)
S1	0.0357 (3)	0.0335 (3)	0.0481 (3)	-0.0054 (2)	-0.0026 (2)	-0.0150 (2)
C11	0.0999 (6)	0.0621 (5)	0.0691 (5)	0.0133 (4)	-0.0379 (5)	-0.0014 (4)
C12	0.0858 (6)	0.0561 (4)	0.1016 (6)	-0.0308 (4)	-0.0391 (5)	-0.0005 (4)

Geometric parameters (Å, °)

C1—C2	1.373 (3)	C14—O3	1.340 (3)
C1—C6	1.383 (3)	C14—C15	1.401 (3)
C1—S1	1.744 (2)	C15—C16	1.411 (3)
C2—C3	1.382 (3)	C15—C19	1.487 (3)
C2—H2	0.9300	C16—C17	1.380 (3)
C3—C4	1.370 (4)	C16—C20	1.488 (3)
C3—H3	0.9300	C17—C18	1.391 (3)
C4—C5	1.370 (4)	C17—H17	0.9300
C4—H4	0.9300	C18—N1	1.414 (3)
C5—C6	1.371 (3)	C19—O4	1.201 (3)
C5—H5	0.9300	C19—H19	0.9300
C6—H6	0.9300	C20—C25	1.383 (3)
C7—C8	1.386 (3)	C20—C21	1.383 (3)
C7—C12	1.392 (3)	C21—C22	1.378 (3)
C7—N1	1.431 (3)	C21—H21	0.9300
C8—C9	1.371 (4)	C22—C23	1.367 (4)
C8—H8	0.9300	C22—H22	0.9300
C9—C10	1.378 (4)	C23—C24	1.367 (4)
C9—H9	0.9300	C23—C11	1.731 (2)
C10—C11	1.376 (3)	C24—C25	1.379 (3)
C10—H10	0.9300	C24—H24	0.9300
C11—C12	1.386 (3)	C25—C12	1.730 (3)
C11—H11	0.9300	N1—S1	1.6557 (19)
C12—C13	1.439 (3)	O1—S1	1.4145 (16)
C13—C18	1.389 (3)	O2—S1	1.4211 (17)
C13—C14	1.390 (3)	O3—H3A	0.826 (10)
C2—C1—C6	120.9 (2)	C14—C15—C19	118.8 (2)
C2—C1—S1	119.29 (17)	C16—C15—C19	121.1 (2)
C6—C1—S1	119.76 (17)	C17—C16—C15	120.9 (2)
C1—C2—C3	119.3 (2)	C17—C16—C20	119.0 (2)
C1—C2—H2	120.4	C15—C16—C20	119.98 (19)
C3—C2—H2	120.4	C16—C17—C18	117.7 (2)
C4—C3—C2	119.7 (2)	C16—C17—H17	121.2
C4—C3—H3	120.2	C18—C17—H17	121.2
C2—C3—H3	120.2	C13—C18—C17	122.80 (19)
C5—C4—C3	120.9 (2)	C13—C18—N1	107.83 (18)
C5—C4—H4	119.6	C17—C18—N1	129.4 (2)
C3—C4—H4	119.6	O4—C19—C15	122.3 (2)
C4—C5—C6	120.0 (2)	O4—C19—H19	118.9

C4—C5—H5	120.0	C15—C19—H19	118.9
C6—C5—H5	120.0	C25—C20—C21	116.9 (2)
C5—C6—C1	119.2 (2)	C25—C20—C16	123.7 (2)
C5—C6—H6	120.4	C21—C20—C16	119.4 (2)
C1—C6—H6	120.4	C22—C21—C20	122.2 (2)
C8—C7—C12	121.5 (2)	C22—C21—H21	118.9
C8—C7—N1	130.3 (2)	C20—C21—H21	118.9
C12—C7—N1	108.20 (18)	C23—C22—C21	118.6 (3)
C9—C8—C7	117.5 (2)	C23—C22—H22	120.7
C9—C8—H8	121.2	C21—C22—H22	120.7
C7—C8—H8	121.2	C22—C23—C24	121.5 (2)
C8—C9—C10	121.8 (2)	C22—C23—C11	119.5 (2)
C8—C9—H9	119.1	C24—C23—C11	119.0 (2)
C10—C9—H9	119.1	C23—C24—C25	118.7 (2)
C11—C10—C9	120.8 (2)	C23—C24—H24	120.7
C11—C10—H10	119.6	C25—C24—H24	120.7
C9—C10—H10	119.6	C24—C25—C20	122.1 (2)
C10—C11—C12	118.7 (2)	C24—C25—C12	117.76 (19)
C10—C11—H11	120.7	C20—C25—C12	120.19 (19)
C12—C11—H11	120.7	C18—N1—C7	107.83 (17)
C11—C12—C7	119.8 (2)	C18—N1—S1	125.70 (15)
C11—C12—C13	132.9 (2)	C7—N1—S1	125.35 (14)
C7—C12—C13	107.26 (19)	C14—O3—H3A	106 (2)
C18—C13—C14	119.19 (19)	O1—S1—O2	120.49 (11)
C18—C13—C12	108.76 (18)	O1—S1—N1	106.41 (10)
C14—C13—C12	132.1 (2)	O2—S1—N1	106.55 (10)
O3—C14—C13	118.5 (2)	O1—S1—C1	108.93 (10)
O3—C14—C15	122.2 (2)	O2—S1—C1	108.09 (10)
C13—C14—C15	119.2 (2)	N1—S1—C1	105.36 (10)
C14—C15—C16	120.03 (19)		
C6—C1—C2—C3	0.8 (4)	C16—C17—C18—C13	-2.0 (3)
S1—C1—C2—C3	-177.4 (2)	C16—C17—C18—N1	179.1 (2)
C1—C2—C3—C4	-0.7 (4)	C14—C15—C19—O4	1.2 (4)
C2—C3—C4—C5	0.0 (4)	C16—C15—C19—O4	179.0 (2)
C3—C4—C5—C6	0.6 (4)	C17—C16—C20—C25	-111.3 (3)
C4—C5—C6—C1	-0.6 (4)	C15—C16—C20—C25	71.2 (3)
C2—C1—C6—C5	-0.1 (3)	C17—C16—C20—C21	69.8 (3)
S1—C1—C6—C5	177.99 (18)	C15—C16—C20—C21	-107.7 (3)
C12—C7—C8—C9	-1.6 (3)	C25—C20—C21—C22	-2.0 (4)
N1—C7—C8—C9	178.3 (2)	C16—C20—C21—C22	176.9 (2)
C7—C8—C9—C10	0.6 (4)	C20—C21—C22—C23	0.4 (4)
C8—C9—C10—C11	1.1 (4)	C21—C22—C23—C24	1.4 (4)
C9—C10—C11—C12	-1.8 (4)	C21—C22—C23—C11	-178.6 (2)
C10—C11—C12—C7	0.9 (3)	C22—C23—C24—C25	-1.3 (4)
C10—C11—C12—C13	-176.5 (2)	C11—C23—C24—C25	178.6 (2)
C8—C7—C12—C11	0.8 (3)	C23—C24—C25—C20	-0.5 (4)
N1—C7—C12—C11	-179.09 (19)	C23—C24—C25—C12	179.5 (2)

C8—C7—C12—C13	178.8 (2)	C21—C20—C25—C24	2.1 (4)
N1—C7—C12—C13	-1.1 (2)	C16—C20—C25—C24	-176.8 (2)
C11—C12—C13—C18	176.4 (2)	C21—C20—C25—C12	-177.94 (19)
C7—C12—C13—C18	-1.2 (2)	C16—C20—C25—C12	3.2 (3)
C11—C12—C13—C14	-3.0 (4)	C13—C18—N1—C7	-3.7 (2)
C7—C12—C13—C14	179.4 (2)	C17—C18—N1—C7	175.4 (2)
C18—C13—C14—O3	177.4 (2)	C13—C18—N1—S1	-172.07 (15)
C12—C13—C14—O3	-3.2 (4)	C17—C18—N1—S1	7.0 (3)
C18—C13—C14—C15	-1.6 (3)	C8—C7—N1—C18	-176.9 (2)
C12—C13—C14—C15	177.8 (2)	C12—C7—N1—C18	3.0 (2)
O3—C14—C15—C16	179.6 (2)	C8—C7—N1—S1	-8.5 (3)
C13—C14—C15—C16	-1.4 (3)	C12—C7—N1—S1	171.39 (15)
O3—C14—C15—C19	-2.6 (3)	C18—N1—S1—O1	-162.99 (18)
C13—C14—C15—C19	176.4 (2)	C7—N1—S1—O1	30.6 (2)
C14—C15—C16—C17	2.9 (3)	C18—N1—S1—O2	-33.2 (2)
C19—C15—C16—C17	-174.9 (2)	C7—N1—S1—O2	160.35 (17)
C14—C15—C16—C20	-179.7 (2)	C18—N1—S1—C1	81.44 (19)
C19—C15—C16—C20	2.5 (3)	C7—N1—S1—C1	-84.97 (19)
C15—C16—C17—C18	-1.2 (3)	C2—C1—S1—O1	135.88 (19)
C20—C16—C17—C18	-178.66 (19)	C6—C1—S1—O1	-42.3 (2)
C14—C13—C18—C17	3.4 (3)	C2—C1—S1—O2	3.3 (2)
C12—C13—C18—C17	-176.1 (2)	C6—C1—S1—O2	-174.85 (17)
C14—C13—C18—N1	-177.47 (19)	C2—C1—S1—N1	-110.30 (19)
C12—C13—C18—N1	3.0 (2)	C6—C1—S1—N1	71.55 (19)

Hydrogen-bond geometry (Å, °)

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O3—H3A...O4	0.83 (1)	1.81 (2)	2.563 (3)	151 (3)
C2—H2...C11 ⁱ	0.93	2.81	3.412 (2)	123
C5—H5...O2 ⁱⁱ	0.93	2.49	3.184 (3)	131

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