



The crystal structure of 6-(4-chlorophenyl)-2-(4-methylbenzyl)imidazo[2,1-*b*][1,3,4]thiadiazole-5-carbaldehyde

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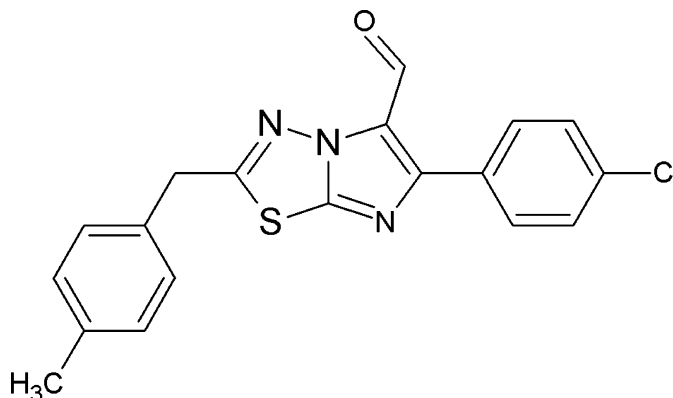
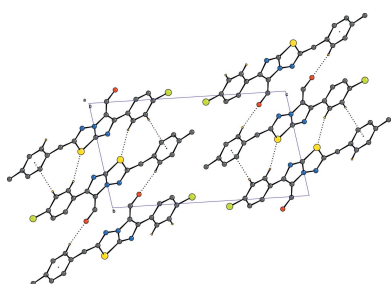
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In the title imidazo[2,1-*b*][1,3,4]thiadiazole derivative, C₁₉H₁₄ClN₃OS, the 4-methylbenzyl and chlorophenyl rings are inclined to the planar imidazo[2,1-*b*][1,3,4]thiadiazole moiety (r.m.s. deviation = 0.012 Å) by 64.5 (1) and 3.7 (1)°, respectively. The molecular structure is primarily stabilized by a strong intramolecular C—H···O hydrogen bond, leading to the formation of a pseudo-seven-membered *S*(7) ring motif, and a short intramolecular C—H···N contact forming an *S*(5) ring motif. In the crystal, molecules are linked by pairs of C—H···S hydrogen bonds, forming inversion dimers. The dimers are linked by C—H···O and C—H··· π interactions, forming chains propagating along [110].

1. Chemical context

The search for potential drugs to fight cancer and the design of molecules with limited side effects, particularly to the immune system, is an emerging area of research. Imidazo[2,1-*b*][1,3,4]thiadiazole derivatives have been reported for their promising biological activities, and the most recent studies indicate their potential as antitumor agents (Karki *et al.*, 2011). However, active heterocyclic pharmacophores particularly at position 5 of the imidazo[2,1-*b*][1,3,4]thiadiazole moiety have shown significant activities; substitution of aldehydes at the 5-position resulted in an improvement of their anticancer activity (Kumar *et al.*, 2014), whereas a substituted phenyl group enhanced the anti-tubercular activity (Ramprasad *et al.*, 2015). In view of the above, we report herein on the synthesis and crystal structure of title imidazo[2,1-*b*][1,3,4]thiadiazole derivative.



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2. Structural commentary

The molecular structure of the title compound is illustrated in Fig. 1. The carbaldehyde group is coplanar with the imidazo-thiadiazole ring system and *cis* to the chlorophenyl ring. Bond C12=O1 is *cis* to the C13–C14 bond, which favours the formation of an intramolecular C15–H15···O1 hydrogen bond (Table 1). The imidazole and thiadiazole rings show different π conjugations, resulting from their fused nature and also due to the groups attached to them. This is evident from the differences in the bond lengths S1–C9 [1.772 (4) Å] and S1–C10 [1.724 (2) Å] of the thiadiazole ring, indicating that the resonance effect caused by the imidazole ring is stronger than that caused by the thiadiazole ring. As a result, the imidazole system is more resonance stabilized. Additionally, the imidazothiadiazole moiety is planar and rigid with maximum deviations of 0.0182 (2) and –0.0078 (3) Å for atoms N2 and C13, respectively, from the mean plane. The 4-chlorophenyl ring makes a dihedral angle of 3.7 (1)°, whereas the 4-methylbenzyl ring is inclined at an angle of 64.5 (1)° with respect to the mean plane of the imidazothiadiazole ring system. The molecular structure is primarily stabilized by the strong intramolecular C15–H15···O1 hydrogen bond, leading to the formation of a pseudo-seven-membered hydrogen-bonded *S*(7) ring motif, and an intramolecular C19–H19···N3 interaction forming an *S*(5) ring motif, thus locking the molecular conformation and eliminating conformational flexibility (Fig. 1 and Table 1).

3. Supramolecular features

In the crystal, the solid-state structure is stabilized primarily by a pair of C–H···S hydrogen bonds, forming inversion dimers (Table 1 and Fig. 2). These dimers are linked by pairs of C–H···O hydrogen bonds and C–H··· π interactions, forming chains propagating along [110]. There are no halogen interactions involving the chlorine atom, and no aromatic π – π stacking interactions present.

4. Database survey

A search of the Cambridge Structural Database (CSD, Version 5.37, last update May 2016; Groom *et al.*, 2016) gave

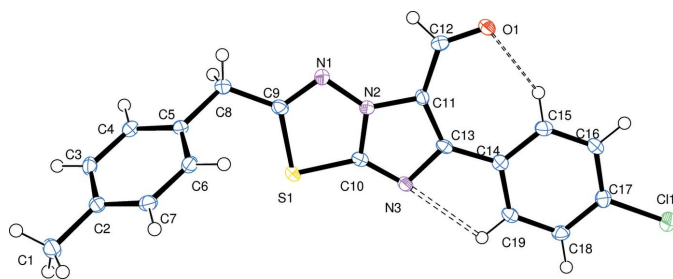


Figure 1

The molecular structure of the title compound, showing the atom labelling. Displacement ellipsoids are drawn at 50% probability level. The intramolecular interactions are shown as dashed lines (see Table 1).

Table 1

Hydrogen-bond geometry (Å, °).

*C*_g is the centroid of the C2–C7 ring.

<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>
C15–H15···O1	0.93	2.20	3.047 (3)	151
C19–H19···N3	0.93	2.42	2.788 (3)	103
C19–H19···S1 ⁱ	0.93	2.83	3.733 (2)	165
C6–H6···O1 ⁱⁱ	0.93	2.46	3.384 (3)	170
C18–H18··· <i>C</i> _g ⁱ	0.93	2.92	3.648 (12)	136

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

55 hits for molecules containing the imidazo[2,1-*b*][1,3,4]-thiadiazole moiety. A search for 2-benzyl-6-phenyl-imidazo[2,1-*b*][1,3,4]thiadiazoles gave ten hits, and five of these compounds contain a 6-phenylimidazo[2,1-*b*][1,3,4]-thiadiazole-5-carbaldehyde moiety. It is interesting to note that the aldehyde group generally accepts a hydrogen bond, and that the *para*-substituted halogens do not generate any significant weak interactions in the crystal packing, except for a C–H···F interaction in 2-(4-fluorobenzyl)-6-phenyl-imidazo[2,1-*b*][1,3,4]thiadiazole-5-carbaldehyde (OWIFAC; Banu *et al.*, 2010), the 4-fluorobenzyl analogue of the title compound.

5. Synthesis and crystallization

The title compound was obtained according to a reported procedure (Kumar *et al.*, 2014). The Vilsmeier reagent was prepared at 273–278 K by adding dropwise phosphorous oxychloride (2.3 g, 15 mmol) into a stirred solution of DMF (10 ml). The 6-(4-chlorophenyl)-2-(4-methylbenzyl) imidazo[2,1-*b*][1,3,4]thiadiazole (4 mmol) was added slowly to the Vilsmeier reagent with stirring and cooling for 2 h. Further stirring was continued for 6 h at 353–363 K. The reaction

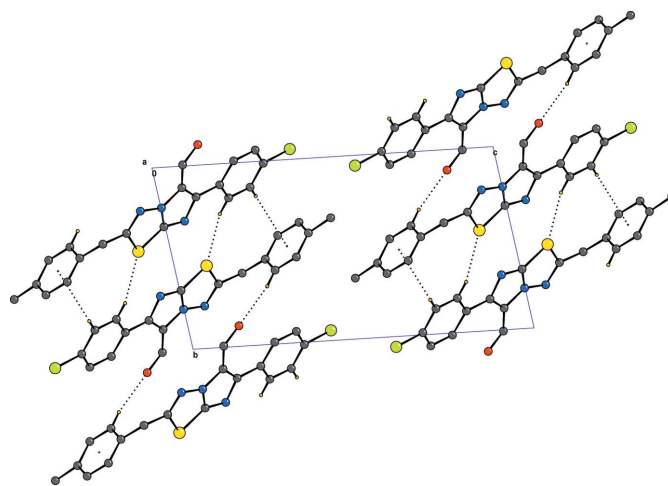


Figure 2

A view along the *a* axis of the crystal packing of the title compound. The intermolecular interactions are shown as dashed lines (see Table 1) and, for clarity, H atoms not involved in these interactions have been omitted.

mixture was then poured into 100 ml of water. The precipitate obtained was filtered, and neutralized with a cold aqueous solution of sodium carbonate. The solid obtained was filtered, washed with water and dried. Single crystals were obtained by slow evaporation of a solution in ethanol/DMF (2:1 v:v).

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. H atoms were positioned geometrically, with N—H = 0.86 Å and C—H = 0.93–0.96 Å, and constrained to ride on their parent atoms with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C-methyl})$ and $1.2U_{\text{eq}}(\text{C,N})$ for other H atoms.

Acknowledgements

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Table 2
Experimental details.

Crystal data	
Chemical formula	C ₁₉ H ₁₄ ClN ₃ OS
M_r	367.84
Crystal system, space group	Triclinic, $P\bar{1}$
Temperature (K)	296
a, b, c (Å)	5.6138 (18), 9.018 (2), 16.514 (5)
α, β, γ (°)	80.533 (13), 87.519 (14), 83.353 (14)
V (Å ³)	818.9 (4)
Z	2
Radiation type	Mo $K\alpha$
μ (mm ⁻¹)	0.37
Crystal size (mm)	0.20 × 0.15 × 0.10
Data collection	
Diffractometer	Bruker <i>SMART</i> CCD area-detector
Absorption correction	Multi-scan (<i>SADABS</i> ; Bruker, 2012)
$T_{\text{min}}, T_{\text{max}}$	0.941, 0.971
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	12059, 2966, 2530
R_{int}	0.059
$(\sin \theta/\lambda)_{\text{max}}$ (Å ⁻¹)	0.606
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.042, 0.110, 1.05
No. of reflections	2966
No. of parameters	228
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å ⁻³)	0.40, -0.26

Computer programs: *SMART* and *SAINT* (Bruker, 2012), *SHELXS97* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2015), *ORTEP-3 for Windows* and *WinGX* (Farrugia, 2012), *CAMERON* (Watkin *et al.*, 1996), *Mercury* (Macrae *et al.*, 2008) and *PLATON* (Spek, 2009).

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The crystal structure of 6-(4-chlorophenyl)-2-(4-methylbenzyl)imidazo[2,1-*b*][1,3,4]thiadiazole-5-carbaldehyde

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Computing details

Data collection: *SMART* (Bruker, 2012); cell refinement: *SAINTE* (Bruker, 2012); data reduction: *SAINTE* (Bruker, 2012); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012), *CAMERON* (Watkin *et al.*, 1996) and *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *WinGX* (Farrugia, 2012) and *PLATON* (Spek, 2009).

6-(4-Chlorophenyl)-2-(4-methylbenzyl)imidazo[2,1-*b*][1,3,4]thiadiazole-5-carbaldehyde

Crystal data

C₁₉H₁₄ClN₃OS

$M_r = 367.84$

Triclinic, *P* $\bar{1}$

Hall symbol: -P 1

$a = 5.6138$ (18) Å

$b = 9.018$ (2) Å

$c = 16.514$ (5) Å

$\alpha = 80.533$ (13)°

$\beta = 87.519$ (14)°

$\gamma = 83.353$ (14)°

$V = 818.9$ (4) Å³

$Z = 2$

$F(000) = 380$

$D_x = 1.492$ Mg m⁻³

Mo *K* α radiation, $\lambda = 0.71073$ Å

Cell parameters from 1890 reflections

$\theta = 3.3$ – 26.4 °

$\mu = 0.37$ mm⁻¹

$T = 296$ K

Block, colourless

$0.20 \times 0.15 \times 0.10$ mm

Data collection

Bruker SMART CCD area-detector
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

ω and ϕ scans

Absorption correction: multi-scan
(SADABS; Bruker, 2012)

$T_{\min} = 0.941$, $T_{\max} = 0.971$

12059 measured reflections

2966 independent reflections

2530 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.059$

$\theta_{\max} = 25.5$ °, $\theta_{\min} = 1.3$ °

$h = -6 \rightarrow 6$

$k = -11 \rightarrow 11$

$l = -20 \rightarrow 20$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.042$

$wR(F^2) = 0.110$

$S = 1.05$

2966 reflections

228 parameters

0 restraints

Hydrogen site location: inferred from
neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0537P)^2 + 0.289P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$

$$\Delta\rho_{\max} = 0.40 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.26 \text{ e } \text{\AA}^{-3}$$

Extinction correction: SHELXL2014
(Sheldrick, 2015)
Extinction coefficient: 0.015 (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.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
S1	0.13628 (9)	0.55026 (6)	0.09398 (3)	0.01783 (18)
Cl1	0.76563 (10)	1.05603 (6)	-0.41113 (3)	0.02857 (19)
O1	-0.2181 (3)	1.11191 (15)	-0.14801 (9)	0.0188 (4)
N1	-0.2122 (3)	0.76902 (19)	0.06190 (10)	0.0169 (4)
N2	-0.0436 (3)	0.77957 (18)	-0.00135 (10)	0.0149 (4)
N3	0.3040 (3)	0.69994 (18)	-0.05952 (10)	0.0158 (4)
C1	0.2608 (4)	0.3316 (3)	0.48434 (13)	0.0254 (5)
H1A	0.3880	0.3909	0.4910	0.038*
H1B	0.3278	0.2319	0.4766	0.038*
H1C	0.1580	0.3249	0.5325	0.038*
C2	0.1165 (4)	0.4061 (2)	0.41000 (12)	0.0182 (5)
C3	-0.0867 (4)	0.3460 (2)	0.38955 (13)	0.0194 (5)
H3	-0.1379	0.2620	0.4234	0.023*
C4	-0.2144 (4)	0.4091 (2)	0.31943 (12)	0.0170 (5)
H4	-0.3490	0.3668	0.3070	0.020*
C5	-0.1425 (4)	0.5349 (2)	0.26779 (12)	0.0164 (5)
C6	0.0587 (4)	0.5973 (2)	0.28907 (13)	0.0187 (5)
H6	0.1082	0.6825	0.2559	0.022*
C7	0.1852 (4)	0.5335 (2)	0.35916 (13)	0.0183 (5)
H7	0.3182	0.5768	0.3722	0.022*
C8	-0.2861 (4)	0.6024 (2)	0.19192 (13)	0.0202 (5)
H8A	-0.3853	0.5279	0.1800	0.024*
H8B	-0.3928	0.6887	0.2045	0.024*
C9	-0.1409 (4)	0.6527 (2)	0.11621 (12)	0.0171 (5)
C10	0.1526 (4)	0.6762 (2)	0.00375 (12)	0.0159 (5)
C11	-0.0221 (4)	0.8823 (2)	-0.07365 (12)	0.0152 (4)
C12	-0.2119 (4)	1.0071 (2)	-0.09103 (13)	0.0174 (5)
H12	-0.3429	1.0065	-0.0545	0.021*
C13	0.1975 (4)	0.8283 (2)	-0.10865 (12)	0.0153 (5)
C14	0.3268 (4)	0.8852 (2)	-0.18484 (12)	0.0157 (4)
C15	0.2369 (4)	1.0111 (3)	-0.24086 (13)	0.0242 (5)
H15	0.0863	1.0608	-0.2313	0.029*
C16	0.3697 (4)	1.0622 (3)	-0.31028 (14)	0.0257 (5)
H16	0.3084	1.1459	-0.3471	0.031*
C17	0.5944 (4)	0.9882 (2)	-0.32487 (13)	0.0198 (5)
C18	0.6866 (4)	0.8621 (2)	-0.27129 (13)	0.0185 (5)

H18	0.8365	0.8122	-0.2816	0.022*
C19	0.5524 (4)	0.8117 (2)	-0.20223 (13)	0.0171 (5)
H19	0.6135	0.7266	-0.1663	0.021*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0166 (3)	0.0178 (3)	0.0168 (3)	0.0008 (2)	-0.0021 (2)	0.0024 (2)
C11	0.0260 (4)	0.0312 (3)	0.0236 (3)	0.0007 (2)	0.0075 (2)	0.0052 (2)
O1	0.0177 (8)	0.0161 (8)	0.0209 (8)	0.0003 (6)	-0.0028 (6)	0.0018 (6)
N1	0.0156 (10)	0.0195 (9)	0.0147 (9)	-0.0018 (7)	-0.0001 (7)	-0.0003 (7)
N2	0.0126 (10)	0.0169 (9)	0.0148 (9)	-0.0014 (7)	-0.0014 (7)	-0.0011 (7)
N3	0.0155 (10)	0.0146 (9)	0.0160 (9)	-0.0001 (7)	-0.0027 (7)	0.0002 (7)
C1	0.0276 (14)	0.0288 (12)	0.0171 (11)	0.0048 (10)	-0.0011 (10)	-0.0007 (9)
C2	0.0189 (12)	0.0200 (11)	0.0138 (10)	0.0065 (8)	0.0032 (9)	-0.0037 (8)
C3	0.0230 (13)	0.0156 (11)	0.0169 (11)	0.0009 (8)	0.0053 (9)	0.0013 (8)
C4	0.0155 (12)	0.0185 (11)	0.0171 (11)	-0.0013 (8)	0.0027 (9)	-0.0044 (8)
C5	0.0141 (12)	0.0188 (11)	0.0146 (10)	0.0026 (8)	0.0008 (8)	-0.0014 (8)
C6	0.0172 (12)	0.0172 (11)	0.0198 (11)	-0.0003 (8)	0.0041 (9)	0.0003 (9)
C7	0.0143 (12)	0.0217 (11)	0.0191 (11)	0.0002 (8)	0.0000 (9)	-0.0051 (9)
C8	0.0140 (12)	0.0238 (12)	0.0205 (11)	-0.0014 (8)	-0.0010 (9)	0.0026 (9)
C9	0.0148 (12)	0.0197 (11)	0.0169 (11)	-0.0012 (8)	-0.0045 (9)	-0.0024 (8)
C10	0.0151 (12)	0.0140 (10)	0.0183 (11)	-0.0002 (8)	-0.0033 (9)	-0.0022 (8)
C11	0.0162 (12)	0.0165 (10)	0.0123 (10)	-0.0026 (8)	-0.0017 (8)	0.0006 (8)
C12	0.0132 (12)	0.0197 (11)	0.0197 (11)	-0.0016 (8)	-0.0012 (9)	-0.0044 (9)
C13	0.0143 (11)	0.0153 (10)	0.0165 (11)	-0.0008 (8)	-0.0062 (8)	-0.0024 (8)
C14	0.0166 (12)	0.0156 (10)	0.0157 (10)	-0.0027 (8)	-0.0027 (8)	-0.0038 (8)
C15	0.0180 (13)	0.0289 (13)	0.0216 (12)	0.0060 (9)	0.0020 (9)	0.0015 (10)
C16	0.0210 (13)	0.0272 (12)	0.0227 (12)	0.0059 (9)	-0.0001 (10)	0.0079 (9)
C17	0.0212 (13)	0.0228 (11)	0.0149 (11)	-0.0023 (9)	0.0003 (9)	-0.0015 (9)
C18	0.0157 (12)	0.0181 (11)	0.0212 (11)	0.0027 (8)	0.0010 (9)	-0.0049 (9)
C19	0.0181 (12)	0.0133 (10)	0.0193 (11)	0.0007 (8)	-0.0033 (9)	-0.0017 (8)

Geometric parameters (Å, °)

S1—C10	1.724 (2)	C5—C8	1.521 (3)
S1—C9	1.772 (2)	C6—C7	1.390 (3)
C11—C17	1.749 (2)	C6—H6	0.9300
O1—C12	1.218 (2)	C7—H7	0.9300
N1—C9	1.299 (3)	C8—C9	1.498 (3)
N1—N2	1.378 (2)	C8—H8A	0.9700
N2—C10	1.355 (3)	C8—H8B	0.9700
N2—C11	1.395 (3)	C11—C13	1.408 (3)
N3—C10	1.323 (3)	C11—C12	1.458 (3)
N3—C13	1.389 (2)	C12—H12	0.9300
C1—C2	1.518 (3)	C13—C14	1.472 (3)
C1—H1A	0.9600	C14—C19	1.401 (3)
C1—H1B	0.9600	C14—C15	1.400 (3)

C1—H1C	0.9600	C15—C16	1.383 (3)
C2—C7	1.390 (3)	C15—H15	0.9300
C2—C3	1.395 (3)	C16—C17	1.388 (3)
C3—C4	1.393 (3)	C16—H16	0.9300
C3—H3	0.9300	C17—C18	1.384 (3)
C4—C5	1.391 (3)	C18—C19	1.382 (3)
C4—H4	0.9300	C18—H18	0.9300
C5—C6	1.401 (3)	C19—H19	0.9300
C10—S1—C9	87.97 (10)	H8A—C8—H8B	107.5
C9—N1—N2	108.08 (16)	N1—C9—C8	122.86 (19)
C10—N2—N1	118.52 (17)	N1—C9—S1	116.07 (16)
C10—N2—C11	108.08 (17)	C8—C9—S1	121.03 (15)
N1—N2—C11	133.36 (17)	N3—C10—N2	113.00 (18)
C10—N3—C13	104.36 (16)	N3—C10—S1	137.61 (15)
C2—C1—H1A	109.5	N2—C10—S1	109.37 (15)
C2—C1—H1B	109.5	N2—C11—C13	103.37 (17)
H1A—C1—H1B	109.5	N2—C11—C12	117.73 (19)
C2—C1—H1C	109.5	C13—C11—C12	138.89 (19)
H1A—C1—H1C	109.5	O1—C12—C11	127.2 (2)
H1B—C1—H1C	109.5	O1—C12—H12	116.4
C7—C2—C3	117.96 (19)	C11—C12—H12	116.4
C7—C2—C1	121.3 (2)	N3—C13—C11	111.17 (18)
C3—C2—C1	120.7 (2)	N3—C13—C14	117.41 (18)
C2—C3—C4	121.3 (2)	C11—C13—C14	131.42 (18)
C2—C3—H3	119.4	C19—C14—C15	117.89 (19)
C4—C3—H3	119.4	C19—C14—C13	118.83 (18)
C5—C4—C3	120.6 (2)	C15—C14—C13	123.27 (19)
C5—C4—H4	119.7	C16—C15—C14	120.7 (2)
C3—C4—H4	119.7	C16—C15—H15	119.6
C4—C5—C6	118.18 (19)	C14—C15—H15	119.6
C4—C5—C8	119.60 (19)	C15—C16—C17	119.9 (2)
C6—C5—C8	122.20 (19)	C15—C16—H16	120.1
C7—C6—C5	120.8 (2)	C17—C16—H16	120.1
C7—C6—H6	119.6	C18—C17—C16	120.8 (2)
C5—C6—H6	119.6	C18—C17—C11	119.38 (17)
C2—C7—C6	121.1 (2)	C16—C17—C11	119.84 (16)
C2—C7—H7	119.4	C19—C18—C17	118.9 (2)
C6—C7—H7	119.4	C19—C18—H18	120.5
C9—C8—C5	115.50 (18)	C17—C18—H18	120.5
C9—C8—H8A	108.4	C18—C19—C14	121.79 (19)
C5—C8—H8A	108.4	C18—C19—H19	119.1
C9—C8—H8B	108.4	C14—C19—H19	119.1
C5—C8—H8B	108.4		
C9—N1—N2—C10	-0.5 (2)	C9—S1—C10—N2	-0.02 (15)
C9—N1—N2—C11	-177.9 (2)	C10—N2—C11—C13	0.5 (2)
C7—C2—C3—C4	1.4 (3)	N1—N2—C11—C13	178.12 (18)

C1—C2—C3—C4	-177.03 (18)	C10—N2—C11—C12	-178.46 (17)
C2—C3—C4—C5	-0.2 (3)	N1—N2—C11—C12	-0.9 (3)
C3—C4—C5—C6	-1.1 (3)	N2—C11—C12—O1	175.43 (19)
C3—C4—C5—C8	-179.56 (19)	C13—C11—C12—O1	-3.1 (4)
C4—C5—C6—C7	1.1 (3)	C10—N3—C13—C11	0.1 (2)
C8—C5—C6—C7	179.56 (19)	C10—N3—C13—C14	179.35 (17)
C3—C2—C7—C6	-1.4 (3)	N2—C11—C13—N3	-0.4 (2)
C1—C2—C7—C6	177.07 (19)	C12—C11—C13—N3	178.2 (2)
C5—C6—C7—C2	0.1 (3)	N2—C11—C13—C14	-179.49 (19)
C4—C5—C8—C9	-139.6 (2)	C12—C11—C13—C14	-0.8 (4)
C6—C5—C8—C9	41.9 (3)	N3—C13—C14—C19	-2.5 (3)
N2—N1—C9—C8	-177.12 (17)	C11—C13—C14—C19	176.5 (2)
N2—N1—C9—S1	0.5 (2)	N3—C13—C14—C15	178.33 (18)
C5—C8—C9—N1	-146.1 (2)	C11—C13—C14—C15	-2.7 (3)
C5—C8—C9—S1	36.4 (3)	C19—C14—C15—C16	-1.1 (3)
C10—S1—C9—N1	-0.27 (17)	C13—C14—C15—C16	178.0 (2)
C10—S1—C9—C8	177.37 (18)	C14—C15—C16—C17	0.0 (4)
C13—N3—C10—N2	0.2 (2)	C15—C16—C17—C18	0.9 (3)
C13—N3—C10—S1	-178.12 (18)	C15—C16—C17—C11	-178.23 (18)
N1—N2—C10—N3	-178.50 (16)	C16—C17—C18—C19	-0.8 (3)
C11—N2—C10—N3	-0.5 (2)	C11—C17—C18—C19	178.40 (15)
N1—N2—C10—S1	0.3 (2)	C17—C18—C19—C14	-0.4 (3)
C11—N2—C10—S1	178.32 (13)	C15—C14—C19—C18	1.3 (3)
C9—S1—C10—N3	178.4 (2)	C13—C14—C19—C18	-177.90 (18)

*Hydrogen-bond geometry (Å, °)*C_g is the centroid of the C2—C7 ring.

<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>
C15—H15...O1	0.93	2.20	3.047 (3)	151
C19—H19...N3	0.93	2.42	2.788 (3)	103
C19—H19...S1 ⁱ	0.93	2.83	3.733 (2)	165
C6—H6...O1 ⁱⁱ	0.93	2.46	3.384 (3)	170
C18—H18...C _g ⁱ	0.93	2.92	3.648 (12)	136

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