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10-Ethynyl-2,3,6,6a,9,10-hexahydro-1*H*-6,9-methanopyrrolo[2,1-*i*][2,1]benzothiazol-10-ol 5,5-dioxide

B. O. Patrick,* H. Liang, S. Canesi and M. A. Ciufolini

Department of Chemistry, University of British Columbia, 2036 Main Mall, Vancouver, BC, Canada V6T 1Z1
Correspondence e-mail: bpatrick@chem.ubc.ca

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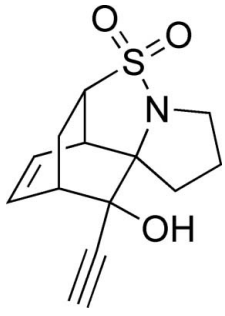
Key indicators: single-crystal X-ray study; T = 173 K; mean σ(C–C) = 0.002 Å; R factor = 0.034; wR factor = 0.095; data-to-parameter ratio = 17.3.

In the title compound, $C_{13}H_{15}NO_3S$, the sole classical hydrogen-bond donor is involved in an intramolecular O—H···N hydrogen bond. In the crystal structure, pairs of molecules related by inversion centres are linked by pairs of weak intermolecular C—H···O interactions; these centrosymmetric pairs are, in turn, linked further by weak intermolecular C—H···O interactions, forming two-dimensional sheets oriented parallel to (101).

Related literature

For background to our ongoing research on the synthesis of himandrine and related alkaloids, see: Ciufolini *et al.* (2007); Liang & Ciufolini (2008).



Experimental

Crystal data

$C_{13}H_{15}NO_3S$ M_r = 265.32
Monoclinic, $C2/c$
a = 24.113 (3) Å
b = 6.6202 (7) Å
c = 15.111 (2) Å
β = 92.625 (5)°
V = 2409.6 (5) Å^3
Z = 8
Mo $K\alpha$ radiation
μ = 0.27 mm^{-1}
T = 173 K
0.35 × 0.27 × 0.18 mm

Data collection

Bruker X8 APEXII diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2008)
T_{min} = 0.877, T_{max} = 0.963
13946 measured reflections
2889 independent reflections
2523 reflections with $I > 2\sigma(I)$
R_{int} = 0.030

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.034
$wR(F^2)$ = 0.095
S = 1.03
2889 reflections
167 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.33 e Å^{-3}
$\Delta\rho_{min}$ = −0.42 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
O9—H9*O*···N13	0.83 (2)	1.99 (2)	2.606 (1)	131 (2)
C8—H8···O16^{i}	1.00	2.53	3.183 (2)	123
C18—H18···O9^{ii}	0.95	2.40	3.341 (2)	169

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

Data collection: *APEX2* (Bruker, 2008); cell refinement: *SAINT* (Bruker, 2008); data reduction: *SAINT*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: LH2908).

References

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supporting information

Acta Cryst. (2009). E**65**, o2621 [https://doi.org/10.1107/S1600536809038410]

10-Ethynyl-2,3,6,6a,9,10-hexahydro-1*H*-6,9-methanopyrrolo[2,1-*i*][2,1]benzothiazol-10-ol 5,5-dioxide

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S1. Comment

The oxidative amidation of phenols offers interesting opportunities in the synthesis of nitrogenous substances. We employed spirocyclization of phenolic sulfonamides to prepare a tricyclic intermediate in the ongoing research on the synthesis of himandrine and related alkaloids (Liang *et al.*, 2008; Ciufolini *et al.*, 2007). The molecular stucture of the title compound is shown in Fig.1. In the crystal structure, pairs of molecules for related by inversion centres are linked by weak intermolecular C—H···O interactions (Table 1, Fig. 2). These centrosymmetric pairs, are in turn, linked further by weak intermolecular C—H···O interactions to form 2-D sheets oriented parallel to the (101) plane, as shown in Fig.3.

S2. Experimental

Potassium carbonate (137 mg, 0.99 mmol) was added to a solution of 10- [(trimethylsilyl)ethynyl]-2,3,6,6a,9,10-hexahydro-1*H*-6,9-methanopyrrolo [2,1-*i*][2,1]benzisothiazol-10-ol 5,5-dioxide (110 mg, 0.33 mmol) in MeOH (1 ml). Upon the completion of the reaction, the mixture was concentrated and dried over high vacuum. Chromatography of the residue (EtOAc / hexanes = 1 / 2) gave 78 mg (0.29 mmol, 89%) product as a colourless solid. X-ray quality single crystals were obtained by slow evaporation of a dichloromethane/hexanes (1:2*v*/*v*) solution of the title compound over two weeks.

S3. Refinement

H atoms boned to C atoms were placed in calculated positions with C-H = 0.93-1.00Å and included in the refinement with U_{iso}(H) = 1.2U_{eq}(C). The hydroxyl H atom was refined indpendently with an isotropic displacement parameter.

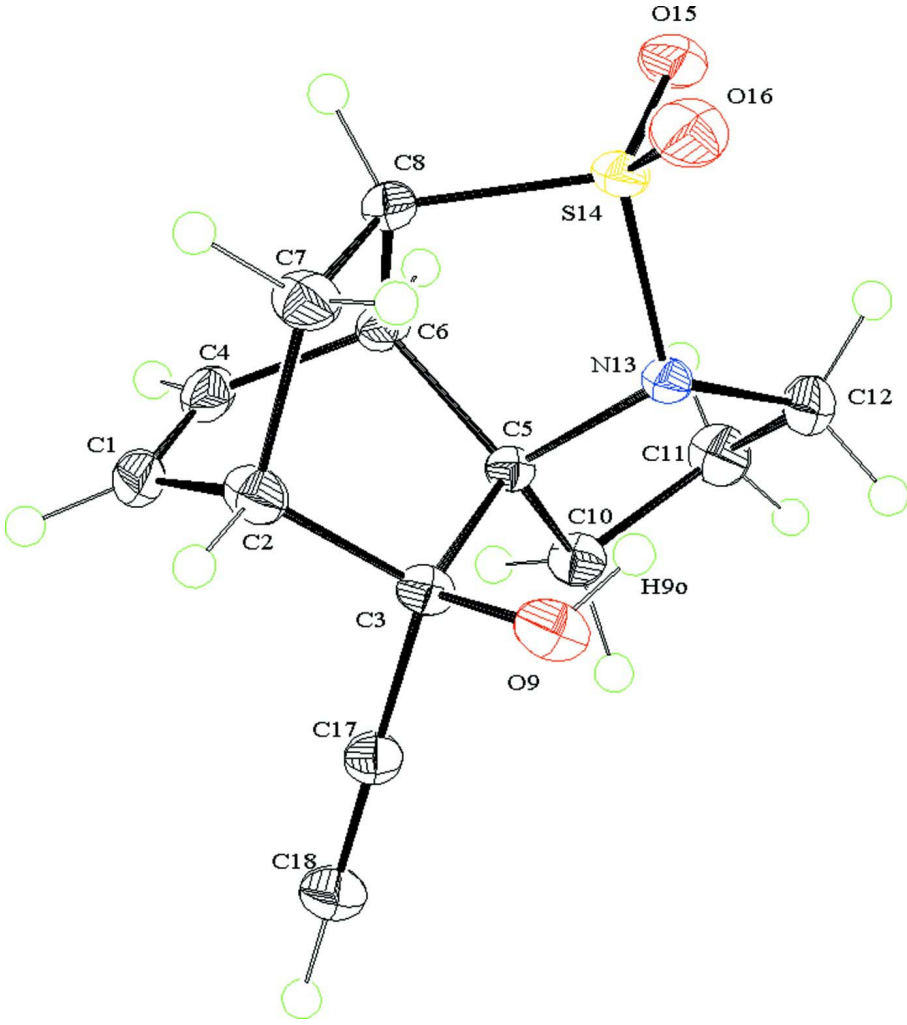

Figure 1

The molecular structure of the title compound, with atom labels and 50% probability displacement ellipsoids for non-H atoms.

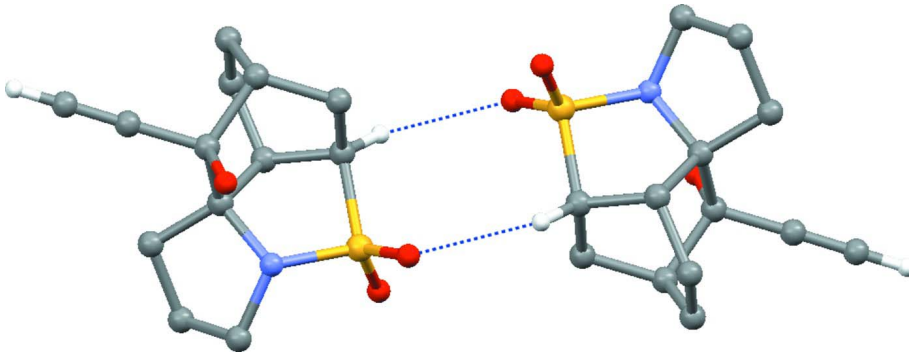

Figure 2

A centrosymmetric pair of molecules with weak intermolecular C—H···O interactions shown as dashed lines.

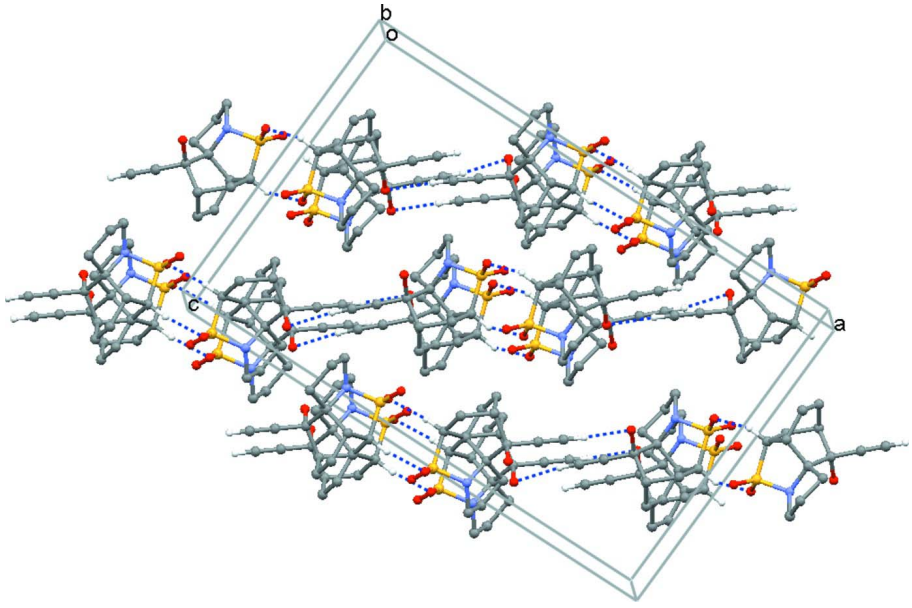

Figure 3

Part of the crystal structure of the title compound, showing C-H···O hydrogen-bonded (dashed lines) sheets parallel to the (101) plane.

10-Ethynyl-2,3,6,6a,9,10-hexahydro-1*H*-6,9- methanopyrrolo[2,1-*i*][2,1]benzothiazol-10-ol 5,5-dioxide

Crystal data

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$M_r = 265.32$
Monoclinic, *C*2/*c*
Hall symbol: -C 2yc
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$b = 6.6202\ (7)$ Å
$c = 15.111\ (2)$ Å
$\beta = 92.625\ (5)°$
$V = 2409.6\ (5)$ Å^3
$Z = 8$
$F(000) = 1120$
$D_x = 1.463$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 6461 reflections
$\theta = 2.7–28.1°$
$\mu = 0.27$ mm^{-1}
$T = 173$ K
Prism, colourless
0.35 × 0.27 × 0.18 mm

Data collection

Bruker X8 APEXII diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2008)
$T_{min} = 0.877$, $T_{max} = 0.963$
13946 measured reflections
2889 independent reflections
2523 reflections with $I > 2\sigma(I)$
$R_{int} = 0.030$
$\theta_{max} = 28.0°$, $\theta_{min} = 1.7°$
$h = -31\rightarrow30$
$k = -7\rightarrow8$
$l = -19\rightarrow19$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.034$
$wR(F^2) = 0.095$
$S = 1.03$
2889 reflections
167 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

$w = 1/[\sigma^2(F_o^2) + (0.0543P)^2 + 1.8974P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.33$ e Å^{-3}
$\Delta\rho_{min} = -0.42$ 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	0.08386 (6)	0.8014 (2)	0.24477 (10)	0.0260 (3)
H1	0.0804	0.8017	0.1819	0.031*
C2	0.10447 (6)	0.6218 (2)	0.29734 (9)	0.0227 (3)
H2	0.1137	0.5077	0.2573	0.027*
C3	0.15678 (6)	0.69210 (19)	0.35283 (9)	0.0167 (3)
C4	0.07087 (6)	0.9590 (2)	0.29339 (10)	0.0241 (3)
H4	0.0580	1.0826	0.2681	0.029*
C5	0.13832 (5)	0.86156 (19)	0.41981 (8)	0.0143 (2)
C6	0.07809 (5)	0.9277 (2)	0.39197 (9)	0.0179 (3)
H6	0.0669	1.0507	0.4252	0.021*
C7	0.05869 (6)	0.5588 (2)	0.36090 (10)	0.0246 (3)
H7A	0.0251	0.5144	0.3261	0.030*
H7B	0.0720	0.4446	0.3985	0.030*
C8	0.04457 (6)	0.7400 (2)	0.41948 (9)	0.0192 (3)
H8	0.0038	0.7682	0.4163	0.023*
C10	0.17913 (6)	1.0368 (2)	0.43416 (9)	0.0197 (3)
H10A	0.2177	0.9926	0.4252	0.024*
H10B	0.1698	1.1497	0.3931	0.024*
C11	0.17199 (6)	1.0997 (2)	0.53035 (10)	0.0258 (3)
H11A	0.2046	1.1761	0.5543	0.031*
H11B	0.1382	1.1827	0.5361	0.031*
C12	0.16678 (6)	0.8971 (2)	0.57668 (9)	0.0238 (3)
H12A	0.2038	0.8389	0.5919	0.029*
H12B	0.1462	0.9112	0.6315	0.029*
C17	0.19816 (6)	0.7687 (2)	0.29199 (9)	0.0187 (3)
C18	0.23235 (6)	0.8204 (2)	0.24254 (10)	0.0237 (3)
H18	0.2597	0.8618	0.2030	0.028*
N13	0.13541 (5)	0.76842 (17)	0.51039 (7)	0.0166 (2)
O9	0.18201 (4)	0.52655 (15)	0.39984 (7)	0.0242 (2)

O15	0.04568 (4)	0.85899 (19)	0.58703 (7)	0.0300 (3)
O16	0.06809 (5)	0.50367 (17)	0.56167 (8)	0.0316 (3)
S14	0.069910 (13)	0.70937 (5)	0.53140 (2)	0.01917 (11)
H9O	0.1739 (10)	0.542 (3)	0.4521 (16)	0.049 (6)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0192 (7)	0.0402 (9)	0.0183 (7)	−0.0073 (6)	−0.0010 (5)	0.0025 (6)
C2	0.0242 (7)	0.0233 (7)	0.0210 (7)	−0.0070 (6)	0.0053 (5)	−0.0054 (5)
C3	0.0182 (6)	0.0136 (6)	0.0187 (6)	0.0007 (5)	0.0044 (5)	0.0015 (5)
C4	0.0178 (6)	0.0313 (8)	0.0228 (7)	0.0008 (6)	−0.0017 (5)	0.0094 (6)
C5	0.0148 (6)	0.0128 (6)	0.0156 (6)	0.0005 (5)	0.0023 (4)	0.0017 (5)
C6	0.0152 (6)	0.0180 (6)	0.0205 (6)	0.0021 (5)	0.0012 (5)	0.0031 (5)
C7	0.0235 (7)	0.0255 (7)	0.0252 (7)	−0.0096 (6)	0.0052 (6)	−0.0040 (6)
C8	0.0149 (6)	0.0239 (7)	0.0188 (6)	−0.0023 (5)	0.0015 (5)	0.0018 (5)
C10	0.0200 (6)	0.0163 (6)	0.0228 (7)	−0.0038 (5)	0.0026 (5)	−0.0006 (5)
C11	0.0277 (7)	0.0236 (7)	0.0261 (7)	−0.0062 (6)	0.0012 (6)	−0.0059 (6)
C12	0.0223 (7)	0.0293 (8)	0.0194 (7)	−0.0024 (6)	−0.0020 (5)	−0.0013 (6)
C17	0.0187 (6)	0.0164 (6)	0.0209 (6)	0.0019 (5)	0.0022 (5)	−0.0003 (5)
C18	0.0231 (7)	0.0232 (7)	0.0252 (7)	−0.0003 (5)	0.0067 (6)	0.0016 (6)
N13	0.0147 (5)	0.0194 (6)	0.0160 (5)	−0.0001 (4)	0.0027 (4)	0.0027 (4)
O9	0.0301 (5)	0.0163 (5)	0.0271 (6)	0.0078 (4)	0.0097 (4)	0.0062 (4)
O15	0.0232 (5)	0.0426 (7)	0.0248 (5)	0.0037 (5)	0.0081 (4)	−0.0073 (5)
O16	0.0286 (6)	0.0307 (6)	0.0357 (6)	−0.0060 (5)	0.0048 (5)	0.0151 (5)
S14	0.01614 (17)	0.0232 (2)	0.01853 (18)	−0.00074 (12)	0.00492 (12)	0.00346 (12)

Geometric parameters (Å, º)

C1—C4	1.322 (2)	C7—H7B	0.9900
C1—C2	1.501 (2)	C8—S14	1.7832 (14)
C1—H1	0.9500	C8—H8	1.0000
C2—C7	1.5532 (19)	C10—C11	1.529 (2)
C2—C3	1.5536 (19)	C10—H10A	0.9900
C2—H2	1.0000	C10—H10B	0.9900
C3—O9	1.4269 (16)	C11—C12	1.521 (2)
C3—C17	1.4770 (18)	C11—H11A	0.9900
C3—C5	1.5882 (17)	C11—H11B	0.9900
C4—C6	1.5062 (19)	C12—N13	1.4938 (18)
C4—H4	0.9500	C12—H12A	0.9900
C5—N13	1.5057 (16)	C12—H12B	0.9900
C5—C10	1.5304 (18)	C17—C18	1.188 (2)
C5—C6	1.5563 (17)	C18—H18	0.9500
C6—C8	1.5497 (18)	N13—S14	1.6716 (11)
C6—H6	1.0000	O9—H9O	0.83 (2)
C7—C8	1.538 (2)	O15—S14	1.4402 (11)
C7—H7A	0.9900	O16—S14	1.4378 (11)

C4—C1—C2	114.33 (13)	C7—C8—C6	109.82 (11)
C4—C1—H1	122.8	C7—C8—S14	112.45 (10)
C2—C1—H1	122.8	C6—C8—S14	100.68 (9)
C1—C2—C7	108.20 (12)	C7—C8—H8	111.2
C1—C2—C3	106.82 (11)	C6—C8—H8	111.2
C7—C2—C3	109.22 (11)	S14—C8—H8	111.2
C1—C2—H2	110.8	C11—C10—C5	103.97 (11)
C7—C2—H2	110.8	C11—C10—H10A	111.0
C3—C2—H2	110.8	C5—C10—H10A	111.0
O9—C3—C17	106.79 (11)	C11—C10—H10B	111.0
O9—C3—C2	110.84 (11)	C5—C10—H10B	111.0
C17—C3—C2	108.77 (11)	H10A—C10—H10B	109.0
O9—C3—C5	110.54 (10)	C12—C11—C10	102.28 (11)
C17—C3—C5	111.79 (10)	C12—C11—H11A	111.3
C2—C3—C5	108.13 (10)	C10—C11—H11A	111.3
C1—C4—C6	114.92 (13)	C12—C11—H11B	111.3
C1—C4—H4	122.5	C10—C11—H11B	111.3
C6—C4—H4	122.5	H11A—C11—H11B	109.2
N13—C5—C10	103.78 (10)	N13—C12—C11	104.12 (11)
N13—C5—C6	106.21 (10)	N13—C12—H12A	110.9
C10—C5—C6	114.26 (11)	C11—C12—H12A	110.9
N13—C5—C3	108.43 (10)	N13—C12—H12B	110.9
C10—C5—C3	115.39 (10)	C11—C12—H12B	110.9
C6—C5—C3	108.17 (10)	H12A—C12—H12B	109.0
C4—C6—C8	109.72 (12)	C18—C17—C3	176.65 (15)
C4—C6—C5	111.73 (11)	C17—C18—H18	180.0
C8—C6—C5	101.16 (10)	C12—N13—C5	109.44 (10)
C4—C6—H6	111.3	C12—N13—S14	117.37 (9)
C8—C6—H6	111.3	C5—N13—S14	110.62 (8)
C5—C6—H6	111.3	C3—O9—H9O	105.3 (16)
C8—C7—C2	109.18 (11)	O16—S14—O15	116.53 (7)
C8—C7—H7A	109.8	O16—S14—N13	108.95 (6)
C2—C7—H7A	109.8	O15—S14—N13	111.24 (6)
C8—C7—H7B	109.8	O16—S14—C8	113.28 (7)
C2—C7—H7B	109.8	O15—S14—C8	110.17 (7)
H7A—C7—H7B	108.3	N13—S14—C8	94.53 (6)

C4—C1—C2—C7	58.42 (16)	C5—C6—C8—C7	−67.18 (13)
C4—C1—C2—C3	−59.07 (15)	C4—C6—C8—S14	169.71 (9)
C1—C2—C3—O9	−175.33 (11)	C5—C6—C8—S14	51.57 (10)
C7—C2—C3—O9	67.86 (14)	N13—C5—C10—C11	−29.30 (13)
C1—C2—C3—C17	−58.21 (14)	C6—C5—C10—C11	85.90 (13)
C7—C2—C3—C17	−175.02 (12)	C3—C5—C10—C11	−147.76 (11)
C1—C2—C3—C5	63.37 (13)	C5—C10—C11—C12	40.51 (14)
C7—C2—C3—C5	−53.44 (14)	C10—C11—C12—N13	−35.77 (14)
C2—C1—C4—C6	−1.13 (18)	O9—C3—C17—C18	35 (3)
O9—C3—C5—N13	−18.73 (14)	C2—C3—C17—C18	−85 (3)
C17—C3—C5—N13	−137.54 (11)	C5—C3—C17—C18	156 (3)

C2—C3—C5—N13	102.76 (11)	C11—C12—N13—C5	18.13 (14)
O9—C3—C5—C10	97.12 (13)	C11—C12—N13—S14	−108.98 (11)
C17—C3—C5—C10	−21.69 (16)	C10—C5—N13—C12	6.98 (13)
C2—C3—C5—C10	−141.39 (11)	C6—C5—N13—C12	−113.80 (12)
O9—C3—C5—C6	−133.51 (11)	C3—C5—N13—C12	130.14 (11)
C17—C3—C5—C6	107.68 (12)	C10—C5—N13—S14	137.81 (9)
C2—C3—C5—C6	−12.02 (13)	C6—C5—N13—S14	17.02 (12)
C1—C4—C6—C8	−55.26 (16)	C3—C5—N13—S14	−99.03 (10)
C1—C4—C6—C5	56.10 (17)	C12—N13—S14—O16	−103.72 (11)
N13—C5—C6—C4	−161.09 (11)	C5—N13—S14—O16	129.74 (9)
C10—C5—C6—C4	85.14 (14)	C12—N13—S14—O15	26.08 (12)
C3—C5—C6—C4	−44.87 (14)	C5—N13—S14—O15	−100.46 (9)
N13—C5—C6—C8	−44.42 (12)	C12—N13—S14—C8	139.77 (10)
C10—C5—C6—C8	−158.19 (11)	C5—N13—S14—C8	13.23 (10)
C3—C5—C6—C8	71.81 (12)	C7—C8—S14—O16	−34.96 (11)
C1—C2—C7—C8	−56.73 (15)	C6—C8—S14—O16	−151.79 (9)
C3—C2—C7—C8	59.20 (15)	C7—C8—S14—O15	−167.50 (9)
C2—C7—C8—C6	3.27 (16)	C6—C8—S14—O15	75.67 (10)
C2—C7—C8—S14	−107.96 (12)	C7—C8—S14—N13	77.91 (10)
C4—C6—C8—C7	50.96 (15)	C6—C8—S14—N13	−38.92 (9)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O9—H9*O*···N13	0.83 (2)	1.99 (2)	2.606 (1)	131 (2)
C8—H8···O16^{i}	1.00	2.53	3.183 (2)	123
C18—H18···O9^{ii}	0.95	2.40	3.341 (2)	169

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