Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

2-[(1,3-Benzothiazol-2-yl)iminomethyl]-6-methoxyphenol: a new monoclinic polymorph

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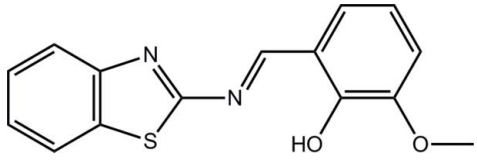
Received 13 July 2013; accepted 13 July 2013

Key indicators: single-crystal X-ray study; T = 100 K; mean σ(C–C) = 0.002 Å; R factor = 0.036; wR factor = 0.095; data-to-parameter ratio = 16.3.

The title compound, $C_{15}H_{12}N_2O_2S$, is a $P2_1/c$ polymorph of a previously reported $P2_1/n$ polymorph [Büyükgüngör *et al.* (2004). *Acta Cryst.* E**60**, o1414–o1416]. The dihedral angle between the benzothiazole (r.m.s. deviation = 0.010 Å) and the benzene ring of 7.86 (6)° compares with 10.76 (10)° in the literature structure. The methoxy substituent is almost coplanar with the benzene ring to which it is attached [C—O—C—C torsion angle = 178.31 (14)°] and the conformation about the imine bond [1.287 (2) Å] is *E*. There is an intramolecular O—H···N hydrogen bond and the hydroxy O and thioether S atoms are *syn*. In the crystal, columns are formed along the *b* axis as centrosymmetric dimeric aggregates, mediated by C—H···O interactions and linked by π–π interactions between the thiazole and benzene rings [centroid-to-centroid distance = 3.8256 (10) Å].

Related literature

For background to the biological activity of organotin compounds with N-, O- and S-atom donors, see: Affan *et al.* (2009). For the structure of the $P2_1/n$ polymorph, see: Büyükgüngör *et al.* (2004).



Experimental

Crystal data

$C_{15}H_{12}N_2O_2S$
M_r = 284.33
Monoclinic, $P2_1/c$
a = 11.6697 (11) Å
b = 6.0250 (6) Å
c = 18.6441 (18) Å
β = 94.346 (1)°
V = 1307.1 (2) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.25 mm^{-1}
T = 100 K
0.20 × 0.16 × 0.15 mm

Data collection

Bruker SMART APEX diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.669, T_{max} = 0.746
15750 measured reflections
2983 independent reflections
2404 reflections with $I > 2\sigma(I)$
R_{int} = 0.046

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.036
$wR(F^2)$ = 0.095
S = 1.05
2983 reflections
183 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.24 e Å^{-3}
$\Delta\rho_{min}$ = −0.26 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1O···N2	0.84	1.88	2.6167 (17)	146
C6—H6···O2^{i}	0.95	2.56	3.424 (2)	151

Symmetry code: (i) $-x+1, -y, -z+1$.

Data collection: *SMART* (Bruker, 2009); cell refinement: *SAINT* (Bruker, 2009); 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 for Windows* (Farrugia, 2012), *QMol* (Gans & Shalloway, 2001) and *DIAMOND* (Brandenburg, 2006); software used to prepare material for publication: *publCIF* (Westrip, 2010).

The authors thank the Natural Sciences and Engineering Council of Canada for support. We also thank the Ministry of Higher Education (Malaysia) for funding structural studies through the High-Impact Research scheme (grant No. UM.C/HIR-MOHE/SC/03).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SU2623).

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supporting information

Acta Cryst. (2013). E**69**, o1273 [doi:10.1107/S1600536813019387]

2-[(1,3-Benzothiazol-2-yl)iminomethyl]-6-methoxyphenol: a new monoclinic polymorph

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S1. Comment

The title compound, (I), was prepared in connection with on-going studies of organotin compounds with *N*, *O* and *S* donors for evaluation for biological activity (Affan *et al.*, 2009).

In (I), Fig. 1, the dihedral angle between the benzothiazole (r.m.s. deviation = 0.010 Å) and the benzene ring is 7.86 (6)°. This, coupled with the observation that the methoxy substituent is coplanar with the benzene ring to which it is attached, the C15—O2—C11—C10 torsion angle is 178.31 (14)°, indicates that the molecule is approximately planar. Indeed, the r.m.s. deviation for all 20 non-hydrogen atoms is 0.083 Å, with maximum deviations of 0.123 (1) Å for the S1 atom and -0.148 (2) Å for C3. As seen from the overlay diagram in Fig. 2, this conformation is similar to that found in the $P2_1/n$ polymorph, for which the dihedral angle between the benzothiazole and benzene ring is 10.76 (10)° (Büyükgüngör *et al.*, 2004). The coplanarity about the imine C8═N2 bond [1.287 (2) Å], with an *E* conformation, enables the formation of an intramolecular O—H···N hydrogen bond, Table 1. The hydroxyl-O and thioether-S atoms are *syn*.

In the crystal packing, centrosymmetrically related molecules associate into dimers *via* C—H···O interactions and stack in columns along the *b* axis *via* *π*–*π* interactions between the thiazole and benzene rings [inter-centroid distance = 3.8256 (10) Å, angle of inclination = 7.47 (8)° for symmetry operation *x*, -1 + *y*, *z*], Fig. 3 and Table 1.

S2. Experimental

2-Aminobenzothiazole (0.765 g, 5 mmol) in ethanol (10 ml) was added to an ethanolic solution of 4-(aminomethyl)-2-methoxyphenol (0.751 g, 5 mmol) and the reaction mixture was refluxed for 2 h. After cooling, a yellow solid was filtered off and washed with cold ethanol. The title compound (I) was obtained after recrystallization from its methanol solution [m.p. 466–468 K, yield 1.18 g (78%)].

S3. Refinement

Carbon-bound H atoms were placed in calculated positions [C—H = 0.95 to 0.98 Å, U_{iso}(H) = 1.5U_{eq}(C-methyl) and 1.2U_{eq}(C) for other H atoms] and were included in the refinement in the riding-model approximation. The hydroxyl H atom was treated similarly [O—H = 0.84 Å; U_{iso}(H) = 1.5U_{eq}(O)].

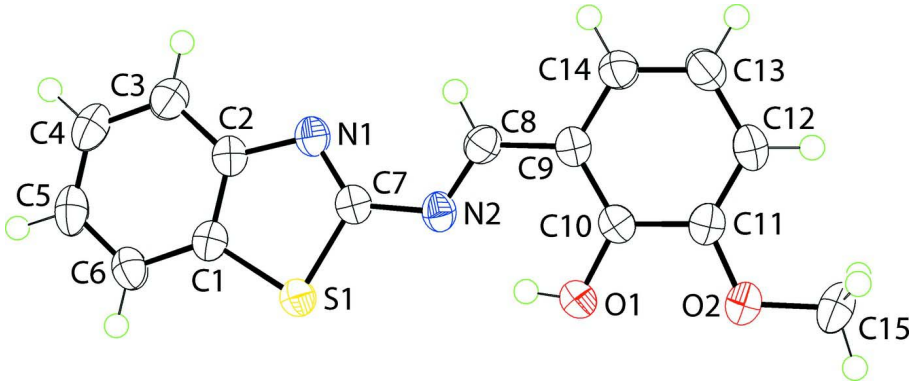

Figure 1

The molecular structure of (I), showing the atom-labelling scheme and displacement ellipsoids at the 70% probability level.

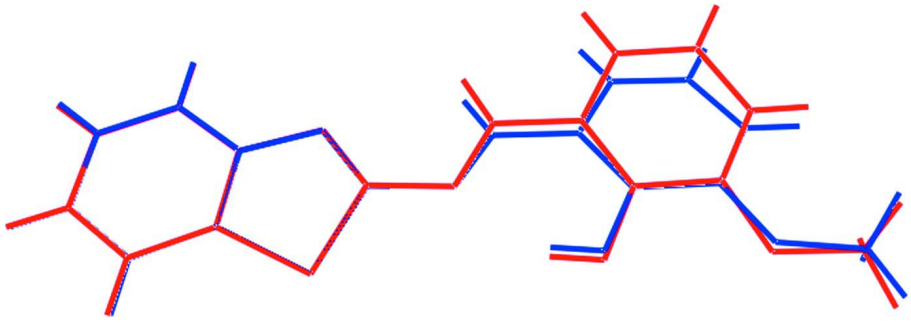

Figure 2

Superimposition of the molecule in (I) (red image) on that found in the polymorph (blue image). The five-membered rings have been superimposed.

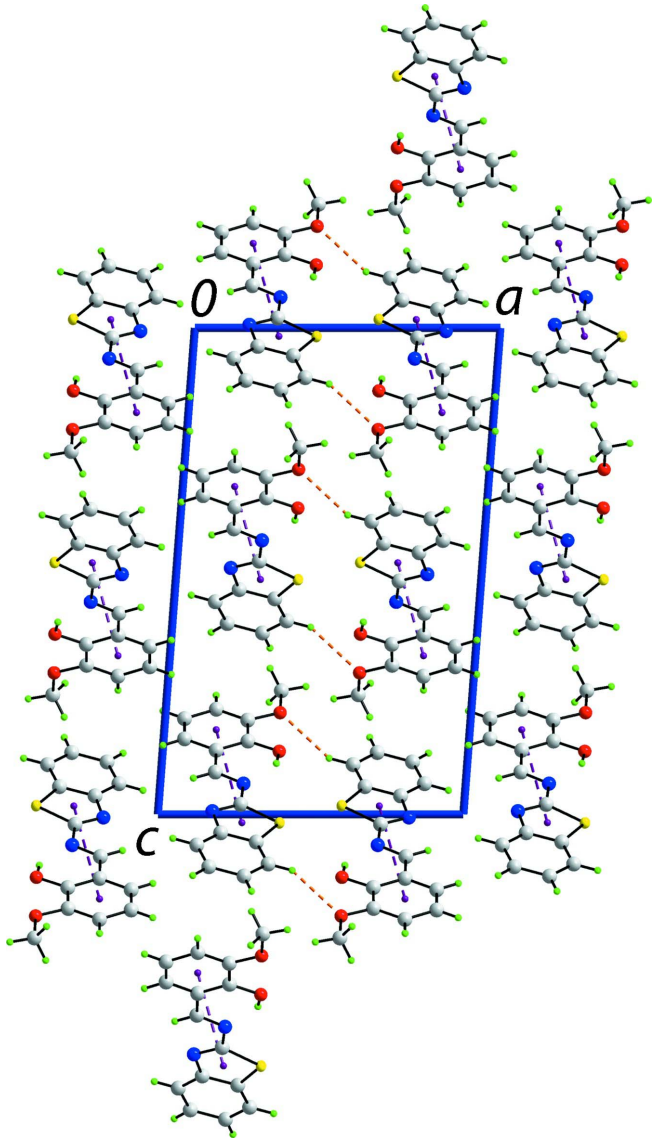

Figure 3

A view in projection down the *b* axis of the unit-cell contents for (I). The C—H···O and π—π interactions are shown as orange and purple dashed lines, respectively.

2-[(1,3-Benzothiazol-2-yl)iminomethyl]-6-methoxyphenol

Crystal data

$C_{15}H_{12}N_2O_2S$
M_r = 284.33
Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc
a = 11.6697 (11) Å
b = 6.0250 (6) Å
c = 18.6441 (18) Å
β = 94.346 (1)°
V = 1307.1 (2) Å^3
Z = 4
$F(000)$ = 592
D_x = 1.445 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 2808 reflections
θ = 2.7–26.6°
μ = 0.25 mm^{-1}
T = 100 K
Block, yellow
0.20 × 0.16 × 0.15 mm

Data collection

Bruker SMART APEX diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.669, T_{max} = 0.746
15750 measured reflections
2983 independent reflections
2404 reflections with $I > 2\sigma(I)$
R_{int} = 0.046
θ_{max} = 27.5°, θ_{min} = 2.2°
h = −15→15
k = −7→7
l = −23→24

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.036
$wR(F^2)$ = 0.095
S = 1.05
2983 reflections
183 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-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0424P)^2 + 0.3573P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.24 e Å^{-3}
$\Delta\rho_{min}$ = −0.26 e Å^{-3}

Special details

Geometry. All s.u.'s (except the s.u. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell s.u.'s are taken into account individually in the estimation of s.u.'s in distances, angles and torsion angles; correlations between s.u.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell s.u.'s is used for estimating s.u.'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 $F^2 > 2\sigma(F^2)$ 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}
S1	0.40036 (3)	−0.28845 (7)	0.51769 (2)	0.02579 (13)
O1	0.38182 (9)	0.30422 (19)	0.37054 (6)	0.0291 (3)
H1O	0.3754	0.1918	0.3966	0.044*
O2	0.37477 (10)	0.6591 (2)	0.29096 (6)	0.0319 (3)
N1	0.17783 (11)	−0.3057 (2)	0.49353 (7)	0.0242 (3)
N2	0.27272 (11)	−0.0044 (2)	0.43688 (7)	0.0233 (3)
C1	0.32893 (13)	−0.5026 (3)	0.55699 (8)	0.0231 (3)
C2	0.21017 (13)	−0.4851 (3)	0.53783 (8)	0.0232 (3)
C3	0.13496 (15)	−0.6425 (3)	0.56295 (9)	0.0301 (4)
H3	0.0549	−0.6355	0.5495	0.036*
C4	0.17954 (16)	−0.8081 (3)	0.60766 (10)	0.0335 (4)
H4	0.1292	−0.9150	0.6257	0.040*
C5	0.29730 (16)	−0.8223 (3)	0.62712 (9)	0.0318 (4)
H5	0.3253	−0.9383	0.6582	0.038*
C6	0.37344 (15)	−0.6718 (3)	0.60217 (9)	0.0278 (4)
H6	0.4535	−0.6826	0.6152	0.033*

C7	0.26852 (13)	−0.1942 (3)	0.47956 (8)	0.0228 (3)
C8	0.17759 (14)	0.0866 (3)	0.41305 (8)	0.0241 (3)
H8	0.1071	0.0233	0.4253	0.029*
C9	0.17491 (13)	0.2822 (3)	0.36818 (8)	0.0225 (3)
C10	0.27665 (13)	0.3830 (3)	0.34943 (8)	0.0221 (3)
C11	0.27064 (14)	0.5760 (3)	0.30645 (8)	0.0235 (3)
C12	0.16509 (14)	0.6647 (3)	0.28398 (8)	0.0265 (4)
H12	0.1612	0.7948	0.2551	0.032*
C13	0.06360 (15)	0.5648 (3)	0.30329 (9)	0.0298 (4)
H13	−0.0088	0.6272	0.2876	0.036*
C14	0.06870 (14)	0.3774 (3)	0.34480 (9)	0.0274 (4)
H14	−0.0004	0.3108	0.3580	0.033*
C15	0.37379 (17)	0.8514 (3)	0.24585 (10)	0.0353 (4)
H15A	0.3302	0.8193	0.2000	0.053*
H15B	0.4529	0.8914	0.2369	0.053*
H15C	0.3377	0.9751	0.2697	0.053*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0245 (2)	0.0231 (2)	0.0297 (2)	0.00138 (16)	0.00111 (16)	0.00382 (17)
O1	0.0241 (6)	0.0283 (7)	0.0344 (7)	0.0017 (5)	−0.0005 (5)	0.0084 (5)
O2	0.0308 (6)	0.0303 (7)	0.0348 (7)	−0.0024 (5)	0.0041 (5)	0.0105 (5)
N1	0.0272 (7)	0.0211 (7)	0.0243 (7)	0.0006 (5)	0.0013 (5)	0.0008 (5)
N2	0.0280 (7)	0.0181 (7)	0.0234 (7)	0.0004 (5)	0.0006 (5)	0.0010 (5)
C1	0.0289 (8)	0.0202 (8)	0.0208 (7)	0.0005 (6)	0.0047 (6)	−0.0015 (6)
C2	0.0293 (8)	0.0198 (8)	0.0206 (7)	0.0020 (6)	0.0036 (6)	−0.0013 (6)
C3	0.0318 (9)	0.0286 (9)	0.0307 (9)	−0.0012 (7)	0.0065 (7)	0.0018 (7)
C4	0.0412 (10)	0.0267 (9)	0.0342 (9)	−0.0031 (8)	0.0122 (8)	0.0049 (7)
C5	0.0466 (11)	0.0239 (9)	0.0257 (9)	0.0065 (8)	0.0075 (8)	0.0051 (7)
C6	0.0327 (9)	0.0264 (9)	0.0244 (8)	0.0060 (7)	0.0027 (7)	0.0016 (7)
C7	0.0263 (8)	0.0210 (8)	0.0209 (8)	0.0015 (6)	0.0008 (6)	−0.0021 (6)
C8	0.0259 (8)	0.0223 (8)	0.0242 (8)	−0.0028 (6)	0.0018 (6)	−0.0014 (6)
C9	0.0272 (8)	0.0201 (8)	0.0199 (7)	0.0001 (6)	0.0000 (6)	−0.0018 (6)
C10	0.0251 (8)	0.0212 (8)	0.0197 (7)	0.0016 (6)	−0.0006 (6)	−0.0028 (6)
C11	0.0293 (8)	0.0209 (8)	0.0203 (7)	−0.0023 (6)	0.0019 (6)	−0.0015 (6)
C12	0.0345 (9)	0.0226 (8)	0.0218 (8)	0.0028 (7)	−0.0014 (7)	0.0024 (6)
C13	0.0288 (9)	0.0290 (9)	0.0310 (9)	0.0046 (7)	−0.0028 (7)	0.0028 (7)
C14	0.0254 (8)	0.0260 (9)	0.0305 (9)	−0.0013 (7)	0.0003 (7)	0.0009 (7)
C15	0.0453 (11)	0.0259 (9)	0.0356 (10)	−0.0051 (8)	0.0092 (8)	0.0063 (8)

Geometric parameters (Å, º)

S1—C1	1.7289 (16)	C5—C6	1.375 (2)
S1—C7	1.7404 (16)	C5—H5	0.9500
O1—C10	1.3466 (18)	C6—H6	0.9500
O1—H1O	0.8400	C8—C9	1.444 (2)
O2—C11	1.3653 (19)	C8—H8	0.9500

O2—C15	1.431 (2)	C9—C10	1.401 (2)
N1—C7	1.296 (2)	C9—C14	1.405 (2)
N1—C2	1.395 (2)	C10—C11	1.411 (2)
N2—C8	1.287 (2)	C11—C12	1.378 (2)
N2—C7	1.396 (2)	C12—C13	1.400 (2)
C1—C6	1.397 (2)	C12—H12	0.9500
C1—C2	1.409 (2)	C13—C14	1.368 (2)
C2—C3	1.397 (2)	C13—H13	0.9500
C3—C4	1.377 (2)	C14—H14	0.9500
C3—H3	0.9500	C15—H15A	0.9800
C4—C5	1.397 (3)	C15—H15B	0.9800
C4—H4	0.9500	C15—H15C	0.9800

C1—S1—C7	88.67 (8)	N2—C8—H8	119.1
C10—O1—H1O	109.5	C9—C8—H8	119.1
C11—O2—C15	116.98 (13)	C10—C9—C14	119.33 (14)
C7—N1—C2	109.40 (13)	C10—C9—C8	121.11 (14)
C8—N2—C7	118.64 (14)	C14—C9—C8	119.53 (15)
C6—C1—C2	121.41 (15)	O1—C10—C9	123.02 (14)
C6—C1—S1	129.12 (13)	O1—C10—C11	117.49 (14)
C2—C1—S1	109.47 (12)	C9—C10—C11	119.50 (14)
C3—C2—N1	125.17 (15)	O2—C11—C12	125.64 (15)
C3—C2—C1	119.68 (15)	O2—C11—C10	114.56 (14)
N1—C2—C1	115.15 (14)	C12—C11—C10	119.80 (15)
C4—C3—C2	118.49 (16)	C11—C12—C13	120.61 (15)
C4—C3—H3	120.8	C11—C12—H12	119.7
C2—C3—H3	120.8	C13—C12—H12	119.7
C3—C4—C5	121.37 (16)	C14—C13—C12	119.95 (15)
C3—C4—H4	119.3	C14—C13—H13	120.0
C5—C4—H4	119.3	C12—C13—H13	120.0
C6—C5—C4	121.34 (16)	C13—C14—C9	120.81 (16)
C6—C5—H5	119.3	C13—C14—H14	119.6
C4—C5—H5	119.3	C9—C14—H14	119.6
C5—C6—C1	117.70 (16)	O2—C15—H15A	109.5
C5—C6—H6	121.1	O2—C15—H15B	109.5
C1—C6—H6	121.1	H15A—C15—H15B	109.5
N1—C7—N2	127.11 (14)	O2—C15—H15C	109.5
N1—C7—S1	117.30 (12)	H15A—C15—H15C	109.5
N2—C7—S1	115.58 (11)	H15B—C15—H15C	109.5
N2—C8—C9	121.88 (15)		

C7—S1—C1—C6	−179.01 (16)	C1—S1—C7—N2	−179.79 (12)
C7—S1—C1—C2	0.03 (12)	C7—N2—C8—C9	−179.54 (13)
C7—N1—C2—C3	−179.18 (15)	N2—C8—C9—C10	−0.8 (2)
C7—N1—C2—C1	0.46 (19)	N2—C8—C9—C14	−178.75 (15)
C6—C1—C2—C3	−1.5 (2)	C14—C9—C10—O1	179.00 (14)
S1—C1—C2—C3	179.37 (12)	C8—C9—C10—O1	1.1 (2)
C6—C1—C2—N1	178.85 (14)	C14—C9—C10—C11	−1.1 (2)

S1—C1—C2—N1	−0.28 (17)	C8—C9—C10—C11	−178.97 (14)
N1—C2—C3—C4	−178.67 (15)	C15—O2—C11—C12	−1.8 (2)
C1—C2—C3—C4	1.7 (2)	C15—O2—C11—C10	178.31 (14)
C2—C3—C4—C5	−0.9 (3)	O1—C10—C11—O2	0.5 (2)
C3—C4—C5—C6	−0.2 (3)	C9—C10—C11—O2	−179.46 (13)
C4—C5—C6—C1	0.5 (2)	O1—C10—C11—C12	−179.39 (14)
C2—C1—C6—C5	0.4 (2)	C9—C10—C11—C12	0.7 (2)
S1—C1—C6—C5	179.32 (13)	O2—C11—C12—C13	−179.97 (15)
C2—N1—C7—N2	179.60 (14)	C10—C11—C12—C13	−0.1 (2)
C2—N1—C7—S1	−0.44 (17)	C11—C12—C13—C14	0.0 (3)
C8—N2—C7—N1	6.8 (2)	C12—C13—C14—C9	−0.4 (3)
C8—N2—C7—S1	−173.12 (12)	C10—C9—C14—C13	0.9 (2)
C1—S1—C7—N1	0.25 (13)	C8—C9—C14—C13	178.87 (15)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1*O*···N2	0.84	1.88	2.6167 (17)	146
C6—H6···O2^{i}	0.95	2.56	3.424 (2)	151

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