Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

(2-Bromophenyl)(4-hydroxy-1,1-dioxo-2*H*-1,2-benzothiazin-3-yl)methanone

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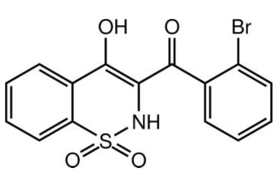
Received 9 March 2012; accepted 27 March 2012

Key indicators: single-crystal X-ray study; T = 173 K; mean σ(C–C) = 0.006 Å; R factor = 0.048; wR factor = 0.106; data-to-parameter ratio = 16.4.

In the title molecule, $C_{15}H_{10}BrNO_4S$, the heterocyclic thiazine ring adopts a half-chair conformation, with the S and N atoms displaced by 0.554 (7) and 0.198 (8) Å, respectively, on opposite sides of the mean plane formed by the remaining ring atoms. The molecular structure is consolidated by intramolecular O—H···O interactions and the crystal packing features N—H···O and C—H···O hydrogen bonds.

Related literature

For the first synthesis of benzothiazine, see: Braun (1923). For background information on the synthesis of related compounds, see: Siddiqui *et al.* (2007). For the biological activity of 1,2-benzothiazine derivatives, see: Lombardino & Wiseman (1972); Gupta *et al.* (1993, 2002); Zia-ur-Rehman *et al.* (2006); Ahmad *et al.* (2010). For related structures, see: Siddiqui *et al.* (2008).



Experimental

Crystal data

$C_{15}H_{10}BrNO_4S$
M_r = 380.21
Monoclinic, $P2_1/c$
a = 12.0433 (4) Å
b = 8.5491 (3) Å
c = 14.7841 (5) Å
β = 106.3950 (19)°
V = 1460.27 (9) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 2.98 mm^{-1}
T = 173 K
0.14 × 0.12 × 0.08 mm

Data collection

Nonius KappaCCD diffractometer
Absorption correction: multi-scan (*SORTAV*; Blessing, 1997)
T_{min} = 0.681, T_{max} = 0.797
6205 measured reflections
3339 independent reflections
2528 reflections with $I > 2\sigma(I)$
R_{int} = 0.043

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.048
$wR(F^2)$ = 0.106
S = 1.10
3339 reflections
203 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.36 e Å^{-3}
$\Delta\rho_{min}$ = −0.61 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1*N*···O4^{i}	0.81 (5)	2.08 (5)	2.861 (4)	160 (4)
C13—H13···O2^{ii}	0.95	2.59	3.305 (5)	132
O3—H3*O*···O4	0.84	1.80	2.530 (4)	145

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

Data collection: *COLLECT* (Hooft, 1998); cell refinement: *DENZO* (Otwinowski & Minor, 1997); data reduction: *SCALEPACK* (Otwinowski & Minor, 1997); 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, 1997); software used to prepare material for publication: *SHELXL97*.

The authors are grateful to the Higher Education Commission, Pakistan, and the Institute of Chemistry, University of the Punjab, Lahore, Pakistan, for financial support.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: AA2054).

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supporting information

Acta Cryst. (2012). E**68**, o1247 [https://doi.org/10.1107/S1600536812013281]

(2-Bromophenyl)(4-hydroxy-1,1-dioxo-2*H*-1,2-benzothiazin-3-yl)methanone

Nazia Sattar, Hamid Latif Siddiqui, Waseeq Ahmad Siddiqui, Muhammad Akram and Masood Parvez

S1. Comment

Since the time first benzothiazine was synthesized (Braun, 1923), thousands of its derivatives have been prepared to determine their pharmacological and other commercial uses. Among nine isomers, the 1,2-benzothiazine 1,1-dioxide nuclei possess dynamic structural features and exhibit a wide range of biological activities, *e.g.*, anti-inflammatory (Lombardino & Wiseman, 1972), analgesic (Gupta *et al.*, 2002), anticancer (Gupta *et al.*, 1993) and antibacterial (Zia-ur-Rehman *et al.*, 2006). In continuation of our research on the synthesis of biologically active benzothiazine derivatives (Siddiqui *et al.*, 2007; Ahmad *et al.*, 2010) herein, we report the synthesis and crystal structure of the title compound.

The bond distances and angles in the title compound (Fig. 1) agree very well with the corresponding bond distances and angles reported in closely related compounds (Siddiqui *et al.*, 2008). The heterocyclic thiazine ring adopts a half chair conformation with atoms N1 and S1 displaced by 0.198 (8) and 0.554 (7) Å, respectively, on the opposite sides from the mean plane formed by the remaining ring atoms. The molecular structure is stabilized by intramolecular hydrogen bonds O3–H3O···O4 and the crystal packing is consolidated by N1—H1N···O4 and C13—H13···O2 intermolecular hydrogen bonds (Fig. 2 and Table 1).

S2. Experimental

A mixture of 2-[2-(*o*-bromophenyl)-2oxoethyl]-1,2-benzisothiazol-3(2*H*)-one 1,1-dioxide (1.8 g, 4.7 mmol) and sodium methoxide (1.9 g, 34.8 mmol) in freshly dried methanol (20 ml) was subjected to reflux for 30 minutes. The reaction was quenched with ice-cold water and acidified to pH = 3 with dilute HCl. The precipitate was filtered, washed with water and ethanol (25 ml, each) to get yellow powder of the title compound (1.3 g, 72%). The crystals suitable for X-ray crystallographic analysis were grown from a mixture of solvents chloroform and methanol (1:2) by slow evaporation at room temperature (m.p. 432–434 K).

S3. Refinement

The H atoms bonded to C and O atoms were positioned geometrically and refined using a riding model, with O—H and C—H = 0.84 and 0.95 Å, respectively. The amino H-atom was allowed to refine freely. The U_{iso}(H) were set at 1.2U_{eq}(parent atom).

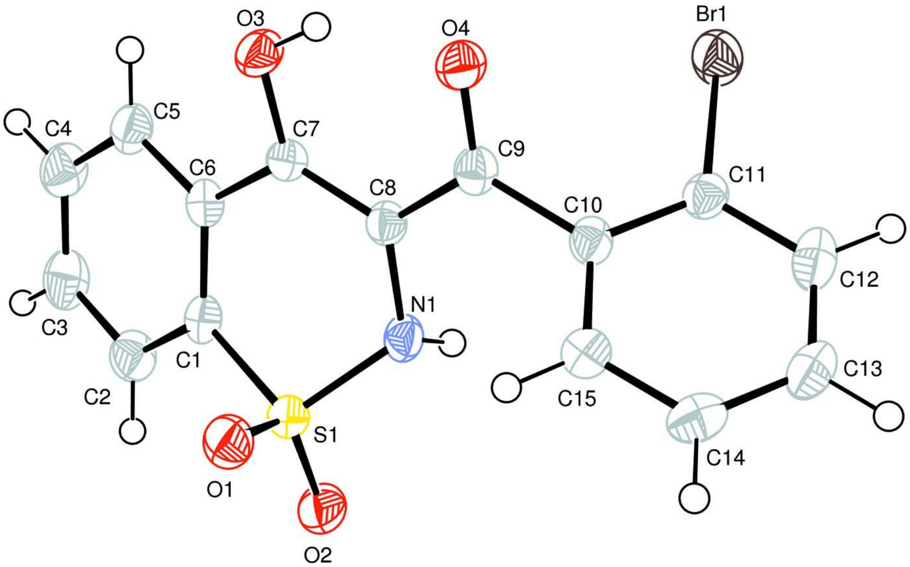

Figure 1

The molecular structure of the title compound with the atom numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms are presented as small spheres of arbitrary radius.

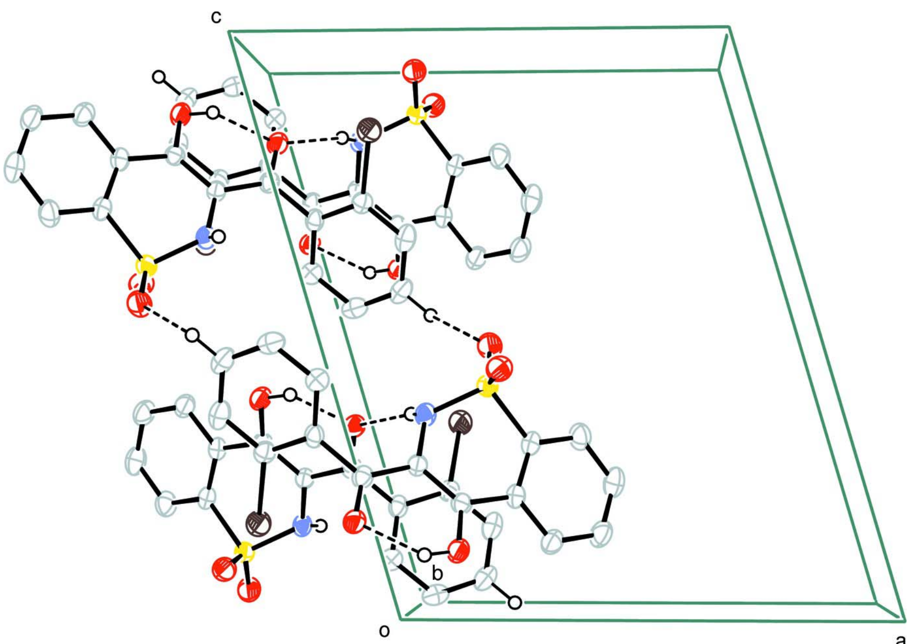

Figure 2

A part of the unit cell showing intermolecular and intramoilecular hydrogen bonds (dotted lines) in the crystal structure of the title compound. H atoms non-participating in hydrogen-bonding were omitted for clarity.

(2-Bromophenyl)(4-hydroxy-1,1-dioxo-2*H*-1,2-benzothiazin-3-yl)methanone

Crystal data

$C_{15}H_{10}BrNO_4S$
M_r = 380.21

Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc

a = 12.0433 (4) Å
b = 8.5491 (3) Å
c = 14.7841 (5) Å
β = 106.3950 (19)°
V = 1460.27 (9) Å^3
Z = 4
F(000) = 760
D_x = 1.729 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 3429 reflections
θ = 1.0–27.5°
μ = 2.98 mm^{-1}
T = 173 K
Prism, pale yellow
0.14 × 0.12 × 0.08 mm

Data collection

Nonius KappaCCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
ω and φ scans
Absorption correction: multi-scan (*SORTAV*; Blessing, 1997)
T_{min} = 0.681, T_{max} = 0.797
6205 measured reflections
3339 independent reflections
2528 reflections with $I > 2\sigma(I)$
R_{int} = 0.043
θ_{max} = 27.6°, θ_{min} = 2.8°
h = −15→15
k = −11→10
l = −19→19

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.048
$wR(F^2)$ = 0.106
S = 1.10
3339 reflections
203 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
$w = 1/[\sigma^2(F_o^2) + (0.0181P)^2 + 4.4694P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ < 0.001
$\Delta\rho_{max}$ = 0.36 e Å^{-3}
$\Delta\rho_{min}$ = −0.61 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 (Å^2)

	x	y	z	U_{iso}*/U_{eq}
Br1	0.27922 (4)	0.40093 (6)	0.66394 (3)	0.03958 (14)
S1	0.81353 (8)	0.40492 (13)	0.89491 (6)	0.0277 (2)
O1	0.8507 (2)	0.2475 (4)	0.9213 (2)	0.0365 (7)
O2	0.8381 (2)	0.5262 (4)	0.9640 (2)	0.0398 (7)
O3	0.6691 (2)	0.2135 (4)	0.62289 (19)	0.0340 (7)
H3O	0.6030	0.1754	0.6166	0.041*
O4	0.4885 (2)	0.1511 (3)	0.67117 (19)	0.0317 (6)
N1	0.6746 (3)	0.4016 (4)	0.8466 (2)	0.0269 (7)

H1N	0.642 (4)	0.484 (5)	0.848 (3)	0.032*
C1	0.8650 (3)	0.4564 (5)	0.7985 (3)	0.0273 (8)
C2	0.9651 (3)	0.5437 (5)	0.8102 (3)	0.0367 (10)
H2	1.0047	0.5867	0.8698	0.044*
C3	1.0058 (4)	0.5666 (6)	0.7323 (3)	0.0415 (11)
H3	1.0734	0.6279	0.7387	0.050*
C4	0.9504 (4)	0.5020 (5)	0.6459 (3)	0.0385 (10)
H4	0.9810	0.5178	0.5940	0.046*
C5	0.8507 (3)	0.4147 (5)	0.6341 (3)	0.0330 (9)
H5	0.8129	0.3709	0.5742	0.040*
C6	0.8057 (3)	0.3911 (5)	0.7107 (3)	0.0264 (8)
C7	0.6983 (3)	0.3029 (5)	0.6993 (3)	0.0241 (8)
C8	0.6335 (3)	0.3124 (5)	0.7626 (3)	0.0249 (8)
C9	0.5241 (3)	0.2322 (5)	0.7435 (3)	0.0262 (8)
C10	0.4524 (3)	0.2456 (5)	0.8110 (3)	0.0262 (8)
C11	0.3407 (3)	0.3076 (5)	0.7837 (3)	0.0267 (8)
C12	0.2732 (4)	0.3111 (5)	0.8461 (3)	0.0374 (10)
H12	0.1979	0.3557	0.8274	0.045*
C13	0.3164 (4)	0.2495 (5)	0.9352 (3)	0.0359 (10)
H13	0.2704	0.2511	0.9779	0.043*
C14	0.4255 (4)	0.1857 (5)	0.9630 (3)	0.0368 (10)
H14	0.4540	0.1419	1.0242	0.044*
C15	0.4942 (4)	0.1852 (5)	0.9020 (3)	0.0328 (9)
H15	0.5703	0.1433	0.9222	0.039*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.0341 (2)	0.0479 (3)	0.0371 (2)	0.0063 (2)	0.01057 (18)	0.0086 (2)
S1	0.0245 (5)	0.0325 (5)	0.0260 (4)	0.0008 (4)	0.0069 (4)	−0.0029 (4)
O1	0.0378 (16)	0.0376 (17)	0.0352 (15)	0.0096 (14)	0.0120 (13)	0.0072 (14)
O2	0.0340 (16)	0.0465 (19)	0.0389 (16)	−0.0021 (14)	0.0102 (13)	−0.0163 (15)
O3	0.0296 (15)	0.0432 (18)	0.0324 (14)	−0.0100 (13)	0.0142 (12)	−0.0119 (14)
O4	0.0300 (14)	0.0371 (17)	0.0300 (14)	−0.0073 (13)	0.0116 (12)	−0.0035 (13)
N1	0.0249 (16)	0.0263 (17)	0.0310 (16)	0.0043 (15)	0.0102 (13)	−0.0028 (15)
C1	0.0242 (18)	0.027 (2)	0.033 (2)	0.0018 (16)	0.0134 (16)	0.0010 (17)
C2	0.029 (2)	0.038 (2)	0.043 (2)	−0.0072 (19)	0.0109 (18)	−0.008 (2)
C3	0.032 (2)	0.042 (3)	0.057 (3)	−0.008 (2)	0.022 (2)	0.000 (2)
C4	0.035 (2)	0.044 (3)	0.042 (2)	−0.005 (2)	0.020 (2)	0.005 (2)
C5	0.032 (2)	0.036 (2)	0.035 (2)	0.0042 (19)	0.0151 (17)	0.0026 (19)
C6	0.0224 (17)	0.025 (2)	0.033 (2)	0.0017 (16)	0.0107 (15)	0.0007 (17)
C7	0.0236 (18)	0.025 (2)	0.0237 (17)	0.0011 (16)	0.0063 (14)	−0.0008 (16)
C8	0.0224 (18)	0.027 (2)	0.0261 (18)	0.0001 (16)	0.0083 (15)	0.0007 (16)
C9	0.0261 (19)	0.026 (2)	0.0285 (18)	0.0013 (16)	0.0102 (15)	0.0036 (17)
C10	0.0230 (18)	0.026 (2)	0.0315 (19)	−0.0055 (16)	0.0100 (15)	−0.0056 (17)
C11	0.0279 (19)	0.025 (2)	0.0281 (19)	−0.0016 (16)	0.0098 (16)	−0.0036 (16)
C12	0.032 (2)	0.036 (2)	0.050 (3)	0.000 (2)	0.021 (2)	−0.005 (2)
C13	0.040 (2)	0.036 (2)	0.038 (2)	−0.004 (2)	0.0227 (19)	−0.005 (2)

C14	0.046 (2)	0.040 (3)	0.026 (2)	−0.002 (2)	0.0127 (18)	0.0008 (19)
C15	0.030 (2)	0.039 (2)	0.030 (2)	0.0002 (19)	0.0095 (17)	−0.0010 (19)

Geometric parameters (Å, º)

Br1—C11	1.892 (4)	C4—H4	0.9500
S1—O2	1.427 (3)	C5—C6	1.401 (5)
S1—O1	1.437 (3)	C5—H5	0.9500
S1—N1	1.623 (3)	C6—C7	1.466 (5)
S1—C1	1.763 (4)	C7—C8	1.378 (5)
O3—C7	1.327 (4)	C8—C9	1.441 (5)
O3—H3O	0.8400	C9—C10	1.498 (5)
O4—C9	1.245 (5)	C10—C11	1.395 (5)
N1—C8	1.423 (5)	C10—C15	1.395 (5)
N1—H1N	0.81 (5)	C11—C12	1.392 (5)
C1—C2	1.387 (5)	C12—C13	1.378 (6)
C1—C6	1.409 (5)	C12—H12	0.9500
C2—C3	1.386 (6)	C13—C14	1.374 (6)
C2—H2	0.9500	C13—H13	0.9500
C3—C4	1.379 (6)	C14—C15	1.385 (5)
C3—H3	0.9500	C14—H14	0.9500
C4—C5	1.382 (6)	C15—H15	0.9500
O2—S1—O1	120.01 (19)	O3—C7—C8	123.1 (3)
O2—S1—N1	107.91 (18)	O3—C7—C6	114.0 (3)
O1—S1—N1	107.86 (19)	C8—C7—C6	122.8 (3)
O2—S1—C1	110.4 (2)	C7—C8—N1	120.0 (3)
O1—S1—C1	107.41 (18)	C7—C8—C9	120.0 (3)
N1—S1—C1	101.73 (18)	N1—C8—C9	119.9 (3)
C7—O3—H3O	109.5	O4—C9—C8	120.5 (3)
C8—N1—S1	117.0 (3)	O4—C9—C10	119.4 (3)
C8—N1—H1N	116 (3)	C8—C9—C10	120.0 (3)
S1—N1—H1N	114 (3)	C11—C10—C15	118.4 (3)
C2—C1—C6	121.6 (4)	C11—C10—C9	121.8 (3)
C2—C1—S1	121.7 (3)	C15—C10—C9	119.7 (3)
C6—C1—S1	116.4 (3)	C12—C11—C10	120.8 (4)
C3—C2—C1	118.1 (4)	C12—C11—Br1	117.6 (3)
C3—C2—H2	120.9	C10—C11—Br1	121.5 (3)
C1—C2—H2	120.9	C13—C12—C11	119.5 (4)
C4—C3—C2	121.4 (4)	C13—C12—H12	120.3
C4—C3—H3	119.3	C11—C12—H12	120.3
C2—C3—H3	119.3	C14—C13—C12	120.6 (4)
C3—C4—C5	120.7 (4)	C14—C13—H13	119.7
C3—C4—H4	119.7	C12—C13—H13	119.7
C5—C4—H4	119.7	C13—C14—C15	120.2 (4)
C4—C5—C6	119.7 (4)	C13—C14—H14	119.9
C4—C5—H5	120.2	C15—C14—H14	119.9
C6—C5—H5	120.2	C14—C15—C10	120.5 (4)

C5—C6—C1	118.5 (4)	C14—C15—H15	119.8
C5—C6—C7	120.8 (4)	C10—C15—H15	119.8
C1—C6—C7	120.7 (3)		

O2—S1—N1—C8	167.0 (3)	C6—C7—C8—N1	−4.8 (6)
O1—S1—N1—C8	−61.9 (3)	O3—C7—C8—C9	−4.8 (6)
C1—S1—N1—C8	50.9 (3)	C6—C7—C8—C9	175.2 (4)
O2—S1—C1—C2	34.0 (4)	S1—N1—C8—C7	−34.1 (5)
O1—S1—C1—C2	−98.5 (4)	S1—N1—C8—C9	145.9 (3)
N1—S1—C1—C2	148.3 (4)	C7—C8—C9—O4	1.6 (6)
O2—S1—C1—C6	−152.1 (3)	N1—C8—C9—O4	−178.4 (4)
O1—S1—C1—C6	75.4 (3)	C7—C8—C9—C10	−178.5 (4)
N1—S1—C1—C6	−37.7 (3)	N1—C8—C9—C10	1.4 (6)
C6—C1—C2—C3	0.3 (6)	O4—C9—C10—C11	−60.3 (5)
S1—C1—C2—C3	173.9 (3)	C8—C9—C10—C11	119.8 (4)
C1—C2—C3—C4	−1.3 (7)	O4—C9—C10—C15	115.1 (4)
C2—C3—C4—C5	1.2 (7)	C8—C9—C10—C15	−64.7 (5)
C3—C4—C5—C6	−0.2 (7)	C15—C10—C11—C12	0.9 (6)
C4—C5—C6—C1	−0.7 (6)	C9—C10—C11—C12	176.4 (4)
C4—C5—C6—C7	178.2 (4)	C15—C10—C11—Br1	177.0 (3)
C2—C1—C6—C5	0.7 (6)	C9—C10—C11—Br1	−7.5 (5)
S1—C1—C6—C5	−173.3 (3)	C10—C11—C12—C13	−1.4 (6)
C2—C1—C6—C7	−178.2 (4)	Br1—C11—C12—C13	−177.7 (3)
S1—C1—C6—C7	7.8 (5)	C11—C12—C13—C14	0.4 (7)
C5—C6—C7—O3	18.6 (5)	C12—C13—C14—C15	1.1 (7)
C1—C6—C7—O3	−162.5 (4)	C13—C14—C15—C10	−1.6 (7)
C5—C6—C7—C8	−161.3 (4)	C11—C10—C15—C14	0.6 (6)
C1—C6—C7—C8	17.5 (6)	C9—C10—C15—C14	−175.0 (4)
O3—C7—C8—N1	175.3 (4)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*N*···O4^{i}	0.81 (5)	2.08 (5)	2.861 (4)	160 (4)
C13—H13···O2^{ii}	0.95	2.59	3.305 (5)	132
O3—H3*O*···O4	0.84	1.80	2.530 (4)	145

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