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Methyl 2-allyl-4-hydroxy-2*H*-1,2-benzothiazine-3-carboxylate 1,1-dioxide

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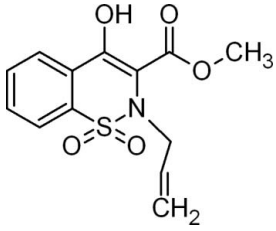
Key indicators: single-crystal X-ray study; T = 296 K; mean σ(C–C) = 0.006 Å; R factor = 0.057; wR factor = 0.103; data-to-parameter ratio = 15.3.

In the title compound, $C_{13}H_{13}NO_5S$, the thiazine ring adopts a distorted half-chair conformation. Intramolecular O—H···O and C—H···O hydrogen bonds give rise to two six-membered hydrogen bonded rings. In the crystal, molecules are linked through weak intermolecular C—H···O hydrogen bonds, resulting in a zigzag chain lying along the c axis.

Related literature

For the syntheses of related compounds, see: Braun (1923); Zia-ur-Rehman *et al.* (2005). For the biological activity of benzothiazines, see: Zia-ur-Rehman *et al.* (2006, 2009). For related structures, see: Arshad *et al.* (2009); Fabiola *et al.* (1998); Zia-ur-Rehman *et al.* (2007).



Experimental

Crystal data

$C_{13}H_{13}NO_5S$
M_r = 295.30
Orthorhombic, $Pca2_1$
a = 12.4289 (10) Å
b = 8.3706 (8) Å
c = 13.0132 (11) Å
V = 1353.9 (2) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.26 mm^{-1}
T = 296 K
0.45 × 0.11 × 0.07 mm

Data collection

Bruker APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.893, T_{max} = 0.982
8404 measured reflections
2808 independent reflections
1763 reflections with $I > 2\sigma(I)$
R_{int} = 0.044

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.057
$wR(F^2)$ = 0.103
S = 1.06
2808 reflections
183 parameters
1 restraint
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.18 e Å^{-3}
$\Delta\rho_{min}$ = −0.23 e Å^{-3}
Absolute structure: Flack (1983), 1046 Friedel pairs
Flack parameter: 0.07 (11)

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

D—H···A	D—H	H···A	D···A	D—H···A
O3—H3*O*···O4	0.82	1.84	2.555 (4)	146
C11—H11*A*···O5	0.97	2.50	3.055 (4)	116
C3—H3*A*···O1^{i}	0.93	2.51	3.406 (6)	163

Symmetry code: (i) $-x-\frac{1}{2}, y, z-\frac{1}{2}$.

Data collection: *APEX2* (Bruker, 2007); cell refinement: *SAINT* (Bruker, 2007); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *PLATON* (Spek, 2009) and *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *WinGX* (Farrugia, 1999) and *PLATON*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: IS2483).

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supporting information

Acta Cryst. (2009). E**65**, o3077 [doi:10.1107/S160053680904673X]

Methyl 2-allyl-4-hydroxy-2*H*-1,2-benzothiazine-3-carboxylate 1,1-dioxide

Muhammad Nadeem Arshad, Muhammad Zia-ur-Rehman and Islam Ullah Khan

S1. Comment

Benzothiazine1,1-dioxides are familiar for their different type of biological activities (Zia-ur-Rehman *et al.*, 2006) and have been synthesized continuously since the very first synthesis in 1923 (Braun, 1923). In continuation of our work on he synthesis of various bioactive benzothiazines (Zia-ur-Rehman *et al.*, 2005, 2009), we herein report the crystal structure of the title compound (**I**), thiazine ring exhibits a distorted half-chair conformation with S1/C1/C6/C7 atoms lying in a plane and N1 showing significant departure from the plane due to its pyramidal geometry projecting the allyl group approximately perpendicular to the ring (Fig. 1). Like previously reported crystal structures of various 1,2-benzothiazine 1,1-dioxide derivatives (Arshad *et al.*, 2009; Fabiola *et al.*, 1998; Zia-ur-Rehman *et al.*, 2007), the enolic hydrogen on O3 is involved in intramolecular hydrogen bonding (Table1). In addition, C11—H11A···O5 hydrogen bond gives rise to another six-membered hydrogen ring in the molecule while C7—C8 bond length [1.338 (5) Å] (very close to normal C—C bond; 1.36 Å) indicates a partial double-bond character indicating the dominance of enolic form in the molecule. The C1—S1 bond distance [1.746 (4) Å] is as expected for typical C(*sp*2)—S bond (1.751 Å). Each molecule is linked to neighbouring molecules *via* weak C—H···O=S interactions giving rise to zigzag chains along the *c* axis (Fig. 2).

S2. Experimental

Allyl iodide (5.04 g, 30.0 mmol) was added drop wise to the mixture of methyl 4-hydroxy-2*H*-1,2-benzothiazine-3-carboxylate-1,1-dioxide (3.83 g, 15.0 mmol), anhydrous potassium carbonate (1.68 g, 30.0 mmol) and dimethyl-formamide (20 ml) in a round bottom flask. Contents were stirred at room temperature for 7 h under nitrogen atmosphere and poured over ice cooled water (300 ml) resulting in an immediate formation of a white solid, which was filtered and washed with cold water. Single crystals were obtained by re-crystallization from a methanol solution

S3. Refinement

All hydrogen atoms were positions geometrically and treated as riding on their parent atoms. The following distances were used: methyl C—H = 0.96 Å, methylene C—H = 0.97 Å, aromatic C—H = 0.93 Å and hydroxyl O—H = 0.82 Å. U_{iso}(H) was set to 1.2U_{eq} of the parent atoms or 1.5U_{eq} for methyl and hydroxyl groups. Large thermal displacement parameters for the terminal carbon atoms (C12 and C13) are observed but the disorder produce was not resolved.

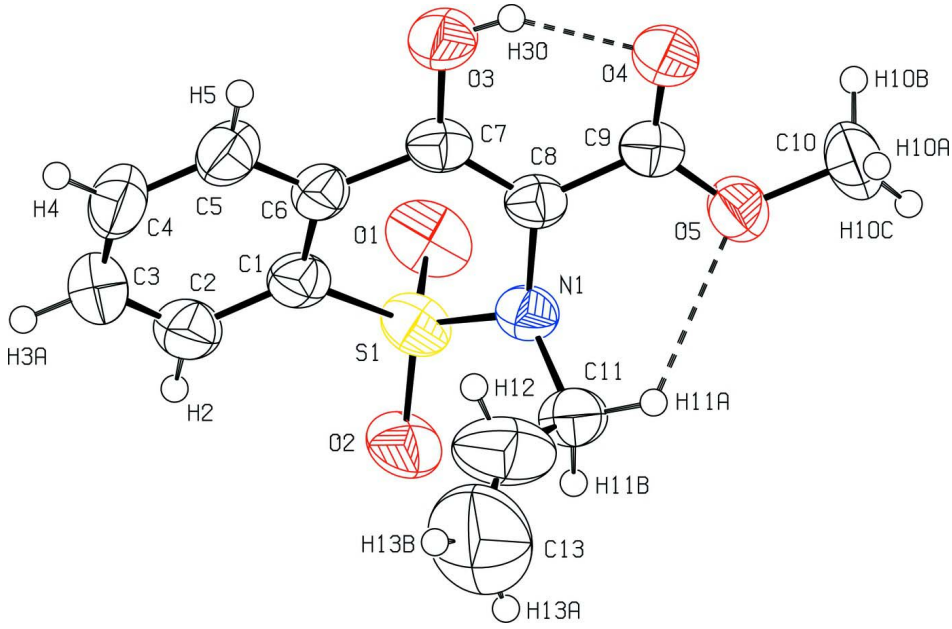

Figure 1

The molecular structure of (**I**), with displacement ellipsoids at the 50% probability level.

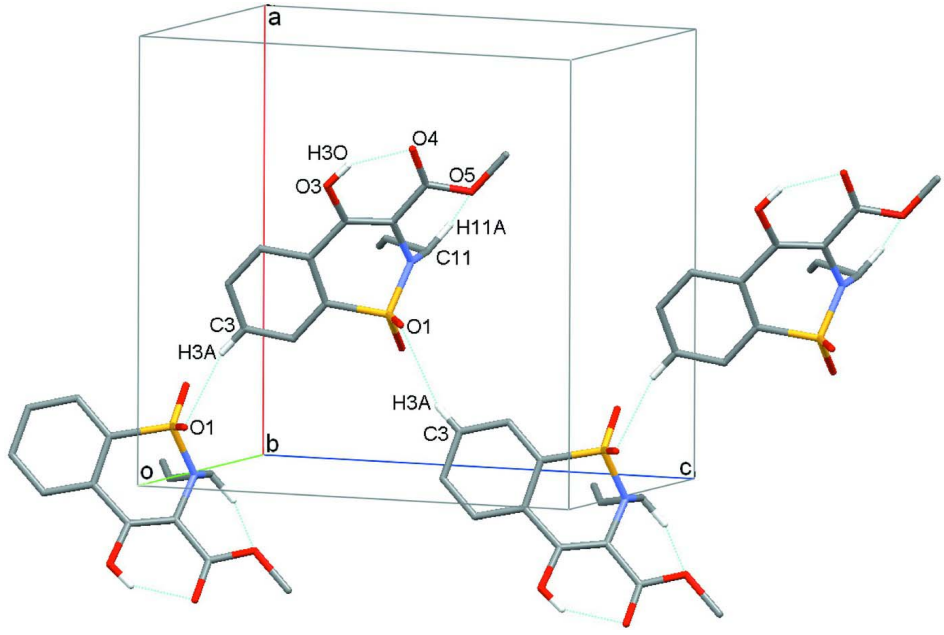

Figure 2

Perspective view of the crystal packing showing O—H···O and C—H···O hydrogen-bonded interactions (dashed lines). H atoms not involved in hydrogen bonding have been omitted for clarity.

Methyl 2-allyl-4-hydroxy-2*H*-1,2-benzothiazine-3-carboxylate 1,1-dioxide

Crystal data

$C_{13}H_{13}NO_5S$
M_r = 295.30

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Hall symbol: P 2c -2ac

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b = 8.3706 (8) Å
c = 13.0132 (11) Å
V = 1353.9 (2) Å^3
Z = 4
F(000) = 616
D_x = 1.449 Mg m^{-3}

Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 1619 reflections
θ = 3.1–21.7°
μ = 0.26 mm^{-1}
T = 296 K
Needle, colourless
0.45 × 0.11 × 0.07 mm

Data collection

Bruker APEXII CCD area-detector diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.893, T_{max} = 0.982

8404 measured reflections
2808 independent reflections
1763 reflections with $I > 2\sigma(I)$
R_{int} = 0.044
θ_{max} = 28.3°, θ_{min} = 2.9°
h = −16→16
k = −11→10
l = −17→9

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.057
$wR(F^2)$ = 0.103
S = 1.06
2808 reflections
183 parameters
1 restraint
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
$w = 1/[\sigma^2(F_o^2) + (0.0381P)^2 + 0.1044P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.18 e Å^{-3}
$\Delta\rho_{min}$ = −0.23 e Å^{-3}
Absolute structure: Flack (1983), 1046 Friedel pairs
Absolute structure parameter: 0.07 (11)

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}
S1	−0.11229 (6)	0.28643 (12)	0.49624 (9)	0.0550 (3)
O1	−0.12270 (18)	0.1530 (4)	0.5634 (3)	0.0733 (9)
O2	−0.19486 (15)	0.4041 (3)	0.4937 (3)	0.0714 (8)
O3	0.18469 (19)	0.0795 (3)	0.4129 (2)	0.0669 (9)
H3O	0.2303	0.0963	0.4571	0.100*
O4	0.26461 (18)	0.2122 (3)	0.5724 (2)	0.0658 (8)
O5	0.16238 (19)	0.3843 (3)	0.6600 (2)	0.0612 (7)
N1	0.0004 (2)	0.3754 (3)	0.5229 (2)	0.0490 (9)

C1	−0.0885 (3)	0.2109 (4)	0.3733 (3)	0.0487 (10)
C2	−0.1708 (3)	0.1997 (5)	0.3013 (4)	0.0647 (12)
H2	−0.2396	0.2360	0.3168	0.078*
C3	−0.1488 (4)	0.1344 (5)	0.2074 (4)	0.0737 (13)
H3A	−0.2034	0.1247	0.1590	0.088*
C4	−0.0462 (4)	0.0828 (5)	0.1837 (4)	0.0721 (12)
H4	−0.0319	0.0406	0.1191	0.087*
C5	0.0348 (3)	0.0935 (5)	0.2553 (3)	0.0602 (12)
H5	0.1032	0.0564	0.2391	0.072*
C6	0.0156 (3)	0.1588 (4)	0.3509 (3)	0.0468 (9)
C7	0.1002 (3)	0.1766 (4)	0.4281 (3)	0.0467 (9)
C8	0.0945 (2)	0.2785 (4)	0.5071 (4)	0.0450 (9)
C9	0.1819 (3)	0.2889 (4)	0.5819 (3)	0.0502 (9)
C10	0.2475 (4)	0.3995 (6)	0.7344 (4)	0.0867 (14)
H10A	0.3070	0.4555	0.7042	0.130*
H10B	0.2706	0.2951	0.7557	0.130*
H10C	0.2218	0.4579	0.7930	0.130*
C11	0.0106 (3)	0.5495 (4)	0.5090 (3)	0.0595 (10)
H11A	0.0695	0.5878	0.5513	0.071*
H11B	−0.0548	0.6004	0.5331	0.071*
C12	0.0304 (4)	0.5986 (7)	0.4006 (5)	0.1008 (19)
H12	0.0732	0.5271	0.3642	0.121*
C13	0.0036 (6)	0.7061 (11)	0.3530 (7)	0.161 (3)
H13A	−0.0395	0.7845	0.3826	0.194*
H13B	0.0249	0.7154	0.2848	0.194*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0376 (4)	0.0683 (6)	0.0593 (6)	0.0050 (4)	0.0069 (5)	0.0078 (7)
O1	0.0553 (15)	0.088 (2)	0.076 (2)	−0.0060 (14)	0.0169 (15)	0.0296 (19)
O2	0.0418 (12)	0.0919 (19)	0.080 (2)	0.0220 (12)	0.0017 (16)	−0.0075 (19)
O3	0.0477 (15)	0.0674 (19)	0.086 (3)	0.0147 (14)	−0.0021 (13)	−0.0186 (15)
O4	0.0474 (14)	0.0682 (17)	0.082 (2)	0.0146 (13)	−0.0103 (13)	−0.0130 (18)
O5	0.0537 (14)	0.0741 (19)	0.0557 (19)	0.0121 (13)	−0.0078 (13)	−0.0097 (16)
N1	0.0439 (14)	0.0501 (18)	0.053 (3)	0.0077 (13)	0.0021 (12)	0.0005 (16)
C1	0.046 (2)	0.037 (2)	0.064 (3)	−0.0039 (16)	−0.0024 (18)	0.006 (2)
C2	0.055 (2)	0.055 (3)	0.084 (4)	0.005 (2)	−0.012 (2)	−0.001 (3)
C3	0.074 (3)	0.072 (3)	0.075 (4)	0.001 (2)	−0.025 (2)	−0.010 (3)
C4	0.092 (3)	0.064 (3)	0.060 (3)	−0.005 (2)	−0.011 (3)	−0.016 (2)
C5	0.057 (2)	0.052 (3)	0.072 (4)	−0.0030 (18)	0.001 (2)	−0.013 (2)
C6	0.0473 (19)	0.039 (2)	0.054 (3)	−0.0024 (15)	−0.0026 (18)	−0.0014 (19)
C7	0.0384 (18)	0.043 (2)	0.059 (3)	0.0018 (15)	0.0066 (18)	0.0058 (19)
C8	0.0376 (15)	0.0445 (19)	0.053 (3)	0.0037 (15)	0.005 (2)	0.001 (2)
C9	0.048 (2)	0.046 (2)	0.057 (3)	0.0034 (18)	0.0015 (19)	0.005 (2)
C10	0.077 (2)	0.113 (4)	0.070 (3)	0.024 (3)	−0.031 (2)	−0.027 (3)
C11	0.061 (2)	0.050 (2)	0.068 (3)	0.0065 (17)	−0.002 (2)	0.001 (2)
C12	0.093 (4)	0.070 (4)	0.139 (6)	0.008 (3)	0.010 (3)	0.036 (4)

C13	0.211 (9)	0.131 (7)	0.142 (7)	−0.031 (6)	−0.035 (6)	0.050 (5)

Geometric parameters (Å, º)

S1—O2	1.423 (2)	C4—C5	1.375 (5)
S1—O1	1.424 (3)	C4—H4	0.9300
S1—N1	1.625 (3)	C5—C6	1.380 (5)
S1—C1	1.746 (4)	C5—H5	0.9300
O3—C7	1.343 (4)	C6—C7	1.462 (5)
O3—H3O	0.8200	C7—C8	1.338 (5)
O4—C9	1.218 (4)	C8—C9	1.461 (5)
O5—C9	1.315 (4)	C10—H10A	0.9600
O5—C10	1.440 (5)	C10—H10B	0.9600
N1—C8	1.438 (4)	C10—H10C	0.9600
N1—C11	1.473 (4)	C11—C12	1.490 (7)
C1—C2	1.390 (5)	C11—H11A	0.9700
C1—C6	1.396 (5)	C11—H11B	0.9700
C2—C3	1.366 (6)	C12—C13	1.142 (8)
C2—H2	0.9300	C12—H12	0.9300
C3—C4	1.380 (6)	C13—H13A	0.9300
C3—H3A	0.9300	C13—H13B	0.9300
O2—S1—O1	119.46 (17)	C1—C6—C7	119.4 (3)
O2—S1—N1	108.03 (15)	C8—C7—O3	122.7 (3)
O1—S1—N1	107.87 (16)	C8—C7—C6	123.7 (3)
O2—S1—C1	110.57 (18)	O3—C7—C6	113.5 (3)
O1—S1—C1	107.1 (2)	C7—C8—N1	120.8 (3)
N1—S1—C1	102.48 (15)	C7—C8—C9	120.7 (3)
C7—O3—H3O	109.5	N1—C8—C9	118.4 (3)
C9—O5—C10	116.0 (3)	O4—C9—O5	123.6 (3)
C8—N1—C11	118.1 (3)	O4—C9—C8	121.9 (4)
C8—N1—S1	114.3 (2)	O5—C9—C8	114.4 (3)
C11—N1—S1	120.1 (2)	O5—C10—H10A	109.5
C2—C1—C6	121.4 (4)	O5—C10—H10B	109.5
C2—C1—S1	121.2 (3)	H10A—C10—H10B	109.5
C6—C1—S1	117.5 (3)	O5—C10—H10C	109.5
C3—C2—C1	118.8 (4)	H10A—C10—H10C	109.5
C3—C2—H2	120.6	H10B—C10—H10C	109.5
C1—C2—H2	120.6	N1—C11—C12	113.8 (4)
C2—C3—C4	120.7 (4)	N1—C11—H11A	108.8
C2—C3—H3A	119.7	C12—C11—H11A	108.8
C4—C3—H3A	119.7	N1—C11—H11B	108.8
C5—C4—C3	120.3 (4)	C12—C11—H11B	108.8
C5—C4—H4	119.9	H11A—C11—H11B	107.7
C3—C4—H4	119.9	C13—C12—C11	133.1 (7)
C4—C5—C6	120.7 (4)	C13—C12—H12	113.5
C4—C5—H5	119.7	C11—C12—H12	113.5
C6—C5—H5	119.7	C12—C13—H13A	120.0

C5—C6—C1	118.1 (3)	C12—C13—H13B	120.0
C5—C6—C7	122.4 (3)	H13A—C13—H13B	120.0
O2—S1—N1—C8	−167.6 (2)	S1—C1—C6—C7	−2.9 (5)
O1—S1—N1—C8	62.0 (3)	C5—C6—C7—C8	159.4 (4)
C1—S1—N1—C8	−50.8 (3)	C1—C6—C7—C8	−19.9 (6)
O2—S1—N1—C11	−18.4 (4)	C5—C6—C7—O3	−21.1 (5)
O1—S1—N1—C11	−148.8 (3)	C1—C6—C7—O3	159.6 (3)
C1—S1—N1—C11	98.4 (3)	O3—C7—C8—N1	−177.3 (3)
O2—S1—C1—C2	−31.7 (4)	C6—C7—C8—N1	2.2 (6)
O1—S1—C1—C2	100.0 (3)	O3—C7—C8—C9	0.0 (6)
N1—S1—C1—C2	−146.6 (3)	C6—C7—C8—C9	179.5 (3)
O2—S1—C1—C6	149.8 (3)	C11—N1—C8—C7	−112.6 (4)
O1—S1—C1—C6	−78.6 (3)	S1—N1—C8—C7	37.3 (4)
N1—S1—C1—C6	34.8 (3)	C11—N1—C8—C9	70.1 (4)
C6—C1—C2—C3	0.8 (6)	S1—N1—C8—C9	−140.1 (3)
S1—C1—C2—C3	−177.7 (3)	C10—O5—C9—O4	2.4 (5)
C1—C2—C3—C4	−1.0 (6)	C10—O5—C9—C8	−179.0 (3)
C2—C3—C4—C5	1.3 (7)	C7—C8—C9—O4	3.8 (6)
C3—C4—C5—C6	−1.3 (6)	N1—C8—C9—O4	−178.8 (3)
C4—C5—C6—C1	1.1 (6)	C7—C8—C9—O5	−174.8 (3)
C4—C5—C6—C7	−178.2 (4)	N1—C8—C9—O5	2.6 (5)
C2—C1—C6—C5	−0.8 (6)	C8—N1—C11—C12	68.0 (4)
S1—C1—C6—C5	177.7 (3)	S1—N1—C11—C12	−80.1 (4)
C2—C1—C6—C7	178.5 (3)	N1—C11—C12—C13	144.7 (8)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H3*O*···O4	0.82	1.84	2.555 (4)	146
C11—H11*A*···O5	0.97	2.50	3.055 (4)	116
C3—H3*A*···O1^{i}	0.93	2.51	3.406 (6)	163

Symmetry code: (i) −*x*−1/2, *y*, *z*−1/2.