IUCrData

ISSN 2414-3146

Ethyl 2-[(5*Z*)-5-(4-methylbenzylidene)-2,4-dioxo-1,3-thiazolidin-3-yl]acetate

Karrouchi Khalid,[a] Hamza Tachallait,[b] Bougrin Khalid,[b] Joel T. Mague[c] and Youssef Ramli[d]*

[a]Laboratoire National de Controle des Médicaments, D M P, Ministère de la Santé, Madinat Al Irfane, BP, Rabat, Morocco, [b]Laboratoire de Chimie des Plantes et de Synthèse Organique et Bioorganique, Faculty of Sciences, Mohammed V University, Rabat, Morocco, [c]Department of Chemistry, Tulane University, New Orleans, LA 70118, USA, and [d]Laboratory of Medicinal Chemistry, Faculty of Medicine and Pharmacy, Mohammed V University, Rabat, Morocco. *Correspondence e-mail: yramli76@yahoo.fr

Received 25 May 2016
Accepted 25 May 2016

Edited by W. T. A. Harrison, University of Aberdeen, Scotland

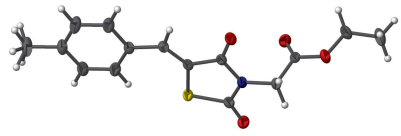
Keywords: crystal structure; thiazolidinone; C—H ···O hydrogen bonds.

CCDC reference: 1481951

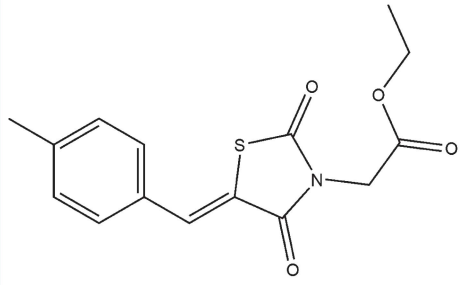
Structural data: full structural data are available from iucrdata.iucr.org

In the title molecule, $C_{15}H_{15}NO_4S$, the dihedral angle between the almost planar heterocyclic ring (r.m.s. deviation = 0.027 Å) and the benzene ring is 5.33 (8)°. The chain of the ester group adopts an extended conformation [C—O—C—C = −174.80 (14)°]. In the crystal, inversion dimers linked by pairs of C—H···O hydrogen bonds generate $R_2^2(10)$ loops and further such bonds connect the dimers into 'stair-step' chains propagating in [100].

3D view



Chemical scheme



Structure description

The 2,4-thiazolidinone ring system is a core structure in various synthetic pharmaceutical agents, displaying a broad spectrum of biological activities such as antidiabetic (Sohda *et al.*, 1992), anticancer (Kaminskyy *et al.*, 2016) and anti-tubercular (Narute *et al.*, 2008) activities. In this study, we report the *N*-alkylation of 5-(4-methylbenzylidene)thiazolidine-2,4-dione, with ethyl bromoacetate, which gave the title compound (Fig. 1) whose crystal structure is reported here.

The molecule exists in an 'extended' conformation with a dihedral angle of 5.3 (1)° between the benzene and heterocyclic rings. In the crystal, pairwise C8—H8···O1^{i} [symmetry code: (i) $-x, -y+1, -z+1$] hydrogen bonds form dimers (Table 1 and Fig. 2), which are further associated by pairwise C12—H12*A*···O3^{ii} [symmetry code: (ii) $x+1, y, z$] into 'stair-step' chains propagating in [100] (Table 1 and Fig. 3).

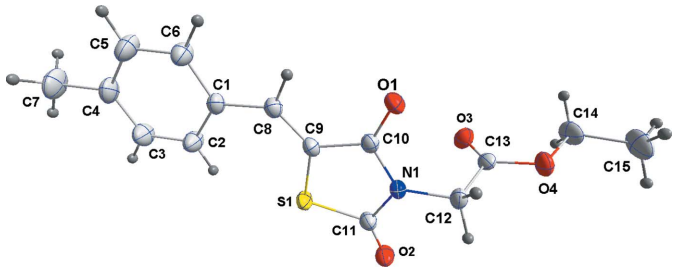


Figure 1
The title molecule with 50% probability ellipsoids.

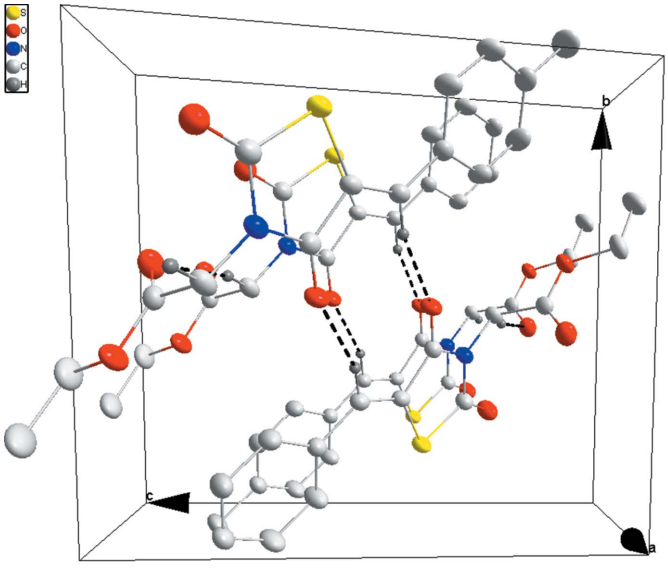


Figure 2
A portion of the packing projected onto (100) showing two dimers connected by C—H···O hydrogen bonds (dotted lines).

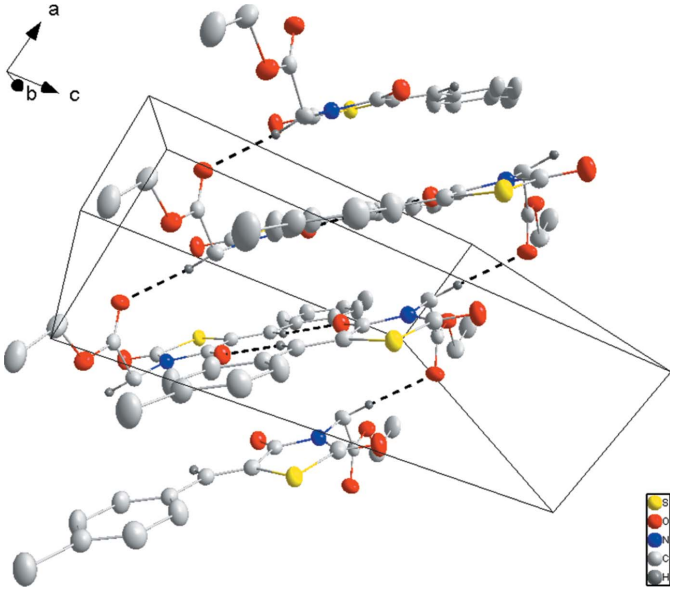


Figure 3
Packing projected onto (1 11 $\bar{4}$) showing a portion of the stepped stack of dimers with C—H···O hydrogen bonds shown as dotted lines.

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

D—H···A	D—H	H···A	D···A	D—H···A
C8—H8···O1^{i}	0.95	2.46	3.3612 (18)	159
C12—H12A···O3^{ii}	0.99	2.31	3.2757 (19)	166

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

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{15}H_{15}NO_4S$
M_r	305.34
Crystal system, space group	Triclinic, $P\overline{1}$
Temperature (K)	150
a, b, c (Å)	4.7310 (1), 11.9082 (3), 13.2907 (4)
α, β, γ (°)	87.354 (1), 82.381 (1), 85.283 (1)
V (Å^3)	739.17 (3)
Z	2
Radiation type	Cu $K\alpha$
μ (mm^{-1})	2.09
Crystal size (mm)	0.19 × 0.08 × 0.08
Data collection	
Diffractometer	Bruker D8 VENTURE PHOTON 100 CMOS
Absorption correction	Multi-scan (*TWINABS*; Sheldrick, 2009)
T_{min}, T_{max}	0.54, 0.85
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	11328, 2825, 2648
R_{int}	0.026
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.625
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.037, 0.096, 1.07
No. of reflections	2825
No. of parameters	192
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.22, −0.27

Computer programs: *APEX3* and *SAINT* (Bruker, 2016), *CELL_NOW* (Sheldrick, 2009), *SHELXT* (Sheldrick, 2015*a*), *SHELXL2014* (Sheldrick, 2015*b*), *DIAMOND* (Brandenburg & Putz, 2012) and *SHELXTL* (Sheldrick, 2008).

Synthesis and crystallization

To a solution of 5-(4-methylbenzylidene)thiazolidine-2,4-dione (1 mmol) in acetone (30 ml), an excess of triethylamine (1.5 mmol) was added and stirred for 10 min at RT. The alkylating agent, ethyl bromoacetate (1.5 mmol), was added slowly. The reaction mixture was then refluxed for 10 h. The progress of reaction was monitored by TLC. The reaction mixture was allowed to attain RT, filtered and concentrated on a rotary evaporator. The residue was dissolved in ethanol. The formed crystals were filtered off, washed with ethanol and recrystallized from ethanol solution. Yield 77%; m.p. 127–129°C.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. Trial refinements using the single-

component reflection extracted with *TWINABS* and the full, two-component data showed the former refinement to be superior. The crystal did not diffract well at high angles, possibly as the result of the twinning. For this reason, the completeness of the data is somewhat less than optimal but, nevertheless, all features of chemical interest are quite satisfactorily determined.

Acknowledgements

The support of NSF-MRI Grant #1228232 for the purchase of the diffractometer and Tulane University for support of the Tulane Crystallography Laboratory are gratefully acknowledged.

References

Brandenburg, K. & Putz, H. (2012). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.
Bruker (2016). *APEX3*, *SAINT* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
Kaminskyy, D., den Hartog, G. J. M., Wojtyra, M., Lelyukh, M., Gzella, A., Bast, A. & Lesyk, R. (2016). *Eur. J. Med. Chem.* **112**, 180–195.
Narute, A., Khedekar, P. & Bhusari, K. (2008). *Ind. J. Chem.* **47**, 586.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Sheldrick, G. M. (2009). *CELL_NOW* and *TWINABS*. University of Göttingen, Germany.
Sheldrick, G. M. (2015*a*). *Acta Cryst.* A**71**, 3–8.
Sheldrick, G. M. (2015*b*). *Acta Cryst.* C**71**, 3–8.
Sohda, T., Mizuno, K., Momose, Y., Ikeda, H., Fujita, T. & Meguro, K. (1992). *J. Med. Chem.* **35**, 2617–2626.

full crystallographic data

IUCrData (2016). **1**, x160851 [doi:10.1107/S2414314616008518]

Ethyl 2-[(5*Z*)-5-(4-methylbenzylidene)-2,4-dioxo-1,3-thiazolidin-3-yl]acetate

Karrouchi Khalid, Hamza Tachallait, Bougrin Khalid, Joel T. Mague and Youssef Ramli

Ethyl 2-[(5*Z*)-5-(4-methylbenzylidene)-2,4-dioxo-1,3-thiazolidin-3-yl]acetate

Crystal data

$C_{15}H_{15}NO_4S$
M_r = 305.34
Triclinic, $P\overline{1}$
a = 4.7310 (1) Å
b = 11.9082 (3) Å
c = 13.2907 (4) Å
α = 87.354 (1)°
β = 82.381 (1)°
γ = 85.283 (1)°
V = 739.17 (3) Å^3
Z = 2
$F(000)$ = 320
D_x = 1.372 Mg m^{-3}
Cu $K\alpha$ radiation, λ = 1.54178 Å
Cell parameters from 5760 reflections
θ = 3.4–74.5°
μ = 2.09 mm^{-1}
T = 150 K
Column, colourless
0.19 × 0.08 × 0.08 mm

Data collection

Bruker D8 VENTURE PHOTON 100 CMOS diffractometer
Radiation source: INCOATEC IμS micro–focus source
Mirror monochromator
Detector resolution: 10.4167 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (*TWINABS*; Sheldrick, 2009)
T_{min} = 0.54, T_{max} = 0.85
11328 measured reflections
2825 independent reflections
2648 reflections with $I > 2\sigma(I)$
R_{int} = 0.026
θ_{max} = 74.5°, θ_{min} = 3.7°
h = −5→5
k = −14→14
l = −15→12

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.037
$wR(F^2)$ = 0.096
S = 1.07
2825 reflections
192 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: mixed
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0496P)^2 + 0.290P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.22 e Å^{-3}
$\Delta\rho_{min}$ = −0.27 e Å^{-3}

Special details

Experimental. Analysis of 1664 reflections having I/σ(I) > 13 and chosen from the full data set with *CELL_NOW* (Sheldrick, 2009) showed the crystal to belong to the triclinic system and to be twinned by a 180° rotation about the *c** axis. The raw data were processed using the multi-component version of *SAINT* under control of the two-component orientation file generated by *CELL_NOW*.

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.

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 $F^2 > 2\text{sigma}(F^2)$ 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. H-atoms attached to carbon were placed in calculated positions (C—H = 0.95 - 0.99 Å) and included as riding contributions with isotropic displacement parameters 1.2 - 1.5 times those of the attached atoms. Trial refinements using the single-component reflection extracted with *TWINABS* and the full, two- component data showed the former refinement to be superior.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
S1	0.46791 (8)	0.80982 (3)	0.58528 (3)	0.02562 (13)	
O1	0.2523 (2)	0.50494 (9)	0.59713 (8)	0.0284 (3)	
O2	0.7768 (3)	0.74899 (10)	0.73387 (9)	0.0338 (3)	
O3	0.1983 (2)	0.55164 (10)	0.85155 (9)	0.0325 (3)	
O4	0.4985 (2)	0.39867 (9)	0.87431 (8)	0.0300 (3)	
N1	0.5379 (3)	0.61154 (10)	0.67263 (9)	0.0233 (3)	
C1	0.0634 (3)	0.78637 (12)	0.39196 (11)	0.0238 (3)	
C2	0.1525 (4)	0.89592 (14)	0.38704 (14)	0.0337 (4)	
H2	0.2683	0.9172	0.4351	0.040*	
C3	0.0744 (4)	0.97353 (14)	0.31324 (14)	0.0362 (4)	
H3	0.1379	1.0473	0.3115	0.043*	
C4	−0.0950 (4)	0.94608 (14)	0.24161 (13)	0.0323 (4)	
C5	−0.1872 (4)	0.83785 (15)	0.24710 (14)	0.0384 (4)	
H5	−0.3059	0.8174	0.1997	0.046*	
C6	−0.1092 (4)	0.75930 (13)	0.32051 (13)	0.0315 (4)	
H6	−0.1742	0.6858	0.3223	0.038*	
C7	−0.1802 (5)	1.03219 (16)	0.16215 (15)	0.0483 (5)	
H7A	−0.1061	1.0093	0.0931	0.072*	0.66 (3)
H7B	−0.3884	1.0447	0.1647	0.072*	0.66 (3)
H7C	−0.1089	1.1058	0.1703	0.072*	0.66 (3)
H7D	−0.2954	1.0010	0.1156	0.072*	0.34 (3)
H7E	−0.0138	1.0611	0.1201	0.072*	0.34 (3)
H7F	−0.2941	1.0976	0.1923	0.072*	0.34 (3)
C8	0.1368 (3)	0.69861 (12)	0.46601 (11)	0.0232 (3)	
H8	0.0588	0.6288	0.4591	0.028*	
C9	0.2959 (3)	0.69950 (11)	0.54241 (11)	0.0220 (3)	
C10	0.3506 (3)	0.59488 (12)	0.60384 (11)	0.0218 (3)	
C11	0.6206 (3)	0.71986 (13)	0.67685 (12)	0.0250 (3)	
C12	0.6377 (3)	0.52013 (13)	0.73800 (11)	0.0250 (3)	
H12A	0.8126	0.5405	0.7640	0.030*	
H12B	0.6885	0.4517	0.6978	0.030*	
C13	0.4152 (3)	0.49421 (12)	0.82666 (11)	0.0224 (3)	
C14	0.3050 (4)	0.36299 (16)	0.96293 (13)	0.0365 (4)	

H14A	0.1216	0.3443	0.9421	0.044*
H14B	0.2651	0.4241	1.0120	0.044*
C15	0.4510 (5)	0.26072 (17)	1.01043 (15)	0.0461 (5)
H15A	0.3232	0.2321	1.0683	0.069*
H15B	0.6272	0.2813	1.0338	0.069*
H15C	0.4976	0.2022	0.9601	0.069*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0323 (2)	0.01908 (19)	0.0270 (2)	−0.00486 (14)	−0.00876 (14)	0.00268 (13)
O1	0.0349 (6)	0.0206 (5)	0.0311 (6)	−0.0083 (4)	−0.0077 (4)	0.0044 (4)
O2	0.0405 (7)	0.0318 (6)	0.0328 (6)	−0.0108 (5)	−0.0152 (5)	0.0030 (5)
O3	0.0259 (6)	0.0396 (6)	0.0299 (6)	0.0046 (5)	−0.0013 (4)	0.0024 (5)
O4	0.0347 (6)	0.0270 (5)	0.0258 (6)	−0.0007 (4)	0.0009 (4)	0.0082 (4)
N1	0.0253 (6)	0.0213 (6)	0.0234 (7)	−0.0027 (5)	−0.0051 (5)	0.0042 (5)
C1	0.0273 (7)	0.0210 (7)	0.0225 (8)	−0.0001 (5)	−0.0030 (6)	0.0009 (5)
C2	0.0427 (9)	0.0247 (8)	0.0373 (9)	−0.0076 (7)	−0.0173 (7)	0.0056 (7)
C3	0.0452 (10)	0.0242 (8)	0.0407 (10)	−0.0062 (7)	−0.0122 (8)	0.0083 (7)
C4	0.0427 (9)	0.0272 (8)	0.0262 (8)	0.0033 (7)	−0.0064 (7)	0.0045 (6)
C5	0.0569 (11)	0.0300 (8)	0.0316 (9)	0.0003 (8)	−0.0212 (8)	0.0000 (7)
C6	0.0442 (9)	0.0217 (7)	0.0306 (9)	−0.0029 (6)	−0.0128 (7)	−0.0001 (6)
C7	0.0719 (14)	0.0365 (10)	0.0374 (11)	0.0028 (9)	−0.0195 (9)	0.0110 (8)
C8	0.0262 (7)	0.0195 (7)	0.0236 (8)	−0.0021 (5)	−0.0027 (5)	0.0008 (5)
C9	0.0245 (7)	0.0176 (6)	0.0233 (7)	−0.0024 (5)	−0.0012 (5)	0.0015 (5)
C10	0.0221 (7)	0.0220 (7)	0.0208 (7)	−0.0023 (5)	−0.0008 (5)	0.0012 (5)
C11	0.0273 (7)	0.0238 (7)	0.0242 (8)	−0.0048 (6)	−0.0030 (6)	0.0018 (5)
C12	0.0241 (7)	0.0247 (7)	0.0250 (8)	0.0007 (5)	−0.0030 (6)	0.0061 (6)
C13	0.0240 (7)	0.0243 (7)	0.0201 (7)	−0.0043 (5)	−0.0061 (5)	0.0005 (5)
C14	0.0418 (9)	0.0432 (10)	0.0238 (9)	−0.0121 (8)	0.0009 (7)	0.0092 (7)
C15	0.0704 (13)	0.0395 (10)	0.0302 (10)	−0.0148 (9)	−0.0113 (9)	0.0136 (8)

Geometric parameters (Å, º)

S1—C9	1.7553 (15)	C5—H5	0.9500
S1—C11	1.7708 (16)	C6—H6	0.9500
O1—C10	1.2140 (18)	C7—H7A	0.9800
O2—C11	1.2066 (19)	C7—H7B	0.9801
O3—C13	1.2025 (18)	C7—H7C	0.9800
O4—C13	1.3329 (18)	C7—H7D	0.9800
O4—C14	1.4619 (19)	C7—H7E	0.9801
N1—C11	1.3840 (19)	C7—H7F	0.9800
N1—C10	1.3858 (19)	C8—C9	1.343 (2)
N1—C12	1.4490 (18)	C8—H8	0.9500
C1—C6	1.396 (2)	C9—C10	1.4816 (19)
C1—C2	1.400 (2)	C12—C13	1.511 (2)
C1—C8	1.455 (2)	C12—H12A	0.9900
C2—C3	1.382 (2)	C12—H12B	0.9900

C2—H2	0.9500	C14—C15	1.505 (3)
C3—C4	1.389 (2)	C14—H14A	0.9900
C3—H3	0.9500	C14—H14B	0.9900
C4—C5	1.390 (2)	C15—H15A	0.9800
C4—C7	1.508 (2)	C15—H15B	0.9800
C5—C6	1.385 (2)	C15—H15C	0.9800

C9—S1—C11	92.06 (7)	H7E—C7—H7F	106.7
C13—O4—C14	115.90 (12)	C9—C8—C1	130.99 (14)
C11—N1—C10	116.74 (12)	C9—C8—H8	114.5
C11—N1—C12	121.85 (12)	C1—C8—H8	114.5
C10—N1—C12	121.40 (12)	C8—C9—C10	119.93 (13)
C6—C1—C2	117.54 (14)	C8—C9—S1	130.02 (11)
C6—C1—C8	117.54 (13)	C10—C9—S1	110.04 (10)
C2—C1—C8	124.92 (14)	O1—C10—N1	122.54 (13)
C3—C2—C1	120.88 (15)	O1—C10—C9	126.79 (13)
C3—C2—H2	119.6	N1—C10—C9	110.67 (12)
C1—C2—H2	119.6	O2—C11—N1	125.07 (14)
C2—C3—C4	121.47 (15)	O2—C11—S1	124.62 (12)
C2—C3—H3	119.3	N1—C11—S1	110.31 (11)
C4—C3—H3	119.3	N1—C12—C13	112.17 (12)
C3—C4—C5	117.82 (15)	N1—C12—H12A	109.2
C3—C4—C7	120.74 (16)	C13—C12—H12A	109.2
C5—C4—C7	121.42 (16)	N1—C12—H12B	109.2
C6—C5—C4	121.16 (16)	C13—C12—H12B	109.2
C6—C5—H5	119.4	H12A—C12—H12B	107.9
C4—C5—H5	119.4	O3—C13—O4	125.07 (14)
C5—C6—C1	121.11 (15)	O3—C13—C12	125.38 (13)
C5—C6—H6	119.4	O4—C13—C12	109.54 (12)
C1—C6—H6	119.4	O4—C14—C15	107.17 (15)
C4—C7—H7A	112.1	O4—C14—H14A	110.3
C4—C7—H7B	112.1	C15—C14—H14A	110.3
H7A—C7—H7B	106.7	O4—C14—H14B	110.3
C4—C7—H7C	112.2	C15—C14—H14B	110.3
H7A—C7—H7C	106.7	H14A—C14—H14B	108.5
H7B—C7—H7C	106.7	C14—C15—H15A	109.5
C4—C7—H7D	112.1	C14—C15—H15B	109.5
C4—C7—H7E	112.1	H15A—C15—H15B	109.5
H7D—C7—H7E	106.7	C14—C15—H15C	109.5
C4—C7—H7F	112.1	H15A—C15—H15C	109.5
H7D—C7—H7F	106.7	H15B—C15—H15C	109.5

C6—C1—C2—C3	−0.7 (3)	C12—N1—C10—C9	−176.67 (12)
C8—C1—C2—C3	179.36 (15)	C8—C9—C10—O1	−4.5 (2)
C1—C2—C3—C4	0.1 (3)	S1—C9—C10—O1	176.30 (13)
C2—C3—C4—C5	0.8 (3)	C8—C9—C10—N1	174.96 (13)
C2—C3—C4—C7	179.48 (18)	S1—C9—C10—N1	−4.26 (15)
C3—C4—C5—C6	−1.0 (3)	C10—N1—C11—O2	178.32 (14)

C7—C4—C5—C6	−179.73 (18)	C12—N1—C11—O2	−0.6 (2)
C4—C5—C6—C1	0.4 (3)	C10—N1—C11—S1	−2.44 (16)
C2—C1—C6—C5	0.5 (2)	C12—N1—C11—S1	178.60 (10)
C8—C1—C6—C5	−179.61 (16)	C9—S1—C11—O2	179.04 (15)
C6—C1—C8—C9	179.98 (16)	C9—S1—C11—N1	−0.21 (11)
C2—C1—C8—C9	−0.1 (3)	C11—N1—C12—C13	101.44 (16)
C1—C8—C9—C10	−176.52 (14)	C10—N1—C12—C13	−77.47 (17)
C1—C8—C9—S1	2.5 (3)	C14—O4—C13—O3	0.5 (2)
C11—S1—C9—C8	−176.60 (15)	C14—O4—C13—C12	179.43 (13)
C11—S1—C9—C10	2.52 (11)	N1—C12—C13—O3	−11.2 (2)
C11—N1—C10—O1	−176.16 (14)	N1—C12—C13—O4	169.83 (12)
C12—N1—C10—O1	2.8 (2)	C13—O4—C14—C15	−174.80 (14)
C11—N1—C10—C9	4.37 (18)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C8—H8···O1^{i}	0.95	2.46	3.3612 (18)	159
C12—H12*A*···O3^{ii}	0.99	2.31	3.2757 (19)	166

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