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Crystal structure of dimethyl 2-((2*Z*,5*Z*)-5-(2-methoxy-2-oxoethylidene)-2-{(*E*)-[2-methyl-5-(prop-1-en-2-yl)cyclohex-2-enylidene]hydrazinylidene}-4-oxothiazolidin-3-yl)fumarate

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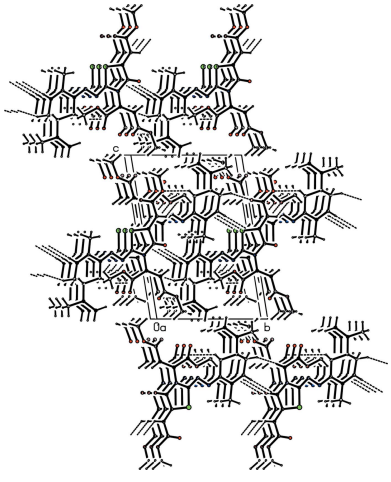
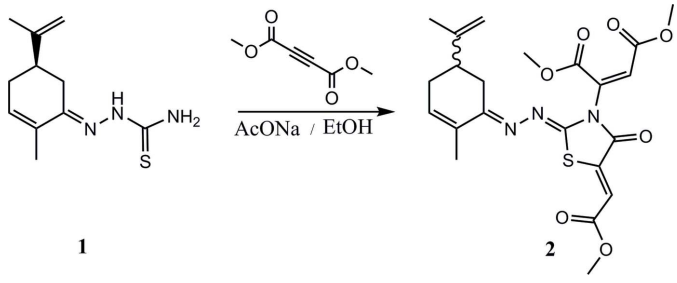
The crystal structure and the conformation of the title compound, $C_{22}H_{27}N_3O_7S$, were determined from the synthetic pathway and by X-ray analysis. This compound is a new 4-thiazolidinone derivative prepared and isolated as pure product from thiosemicarbazone carvone. The molecule is built up from an oxothiazolidine ring tetrasubstituted by a methoxy–oxoethylidene, a maleate, an oxygen and a cyclohexylidene–hydrazone. The cyclohexylidene ring is statistically disordered over two positions, resulting in an inversion of configuration for the substituted carbon.

1. Chemical context

In recent years, the synthesis of heterocyclic systems containing nitrogen and sulfur has attracted great interest because of their broad spectrum of pharmacological activities. The thiazol nucleus is found in a large number of natural products (Nielsen *et al.*, 2012), as well as in diverse pharmaceutical products (Le Flohic *et al.*, 2005). Indeed, some 4-arylthiazole derivatives exhibit a strong anti-inflammatory activity (Hirai & Sugimoto, 1977) while some tetrahydrothiazolo-[4,5-*b*] pyridines show antioxidant properties (Uchikawa *et al.*, 1996). The therapeutic usefulness of these heterocyclic systems prompted us to prepare a new substituted thiazole which shows important medicinal properties. The title compound **2** was synthesized by the reaction of (*R*)-thiosemicarbazone carvone **1** easily obtained from naturally occurring (*R*)-carvone] with dimethyl acetylenedicarboxylate in basic medium, using ethanol as solvent. The resulting product **2** was obtained in 65% yield.





1 **2**

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

D—H···A	D—H	H···A	D···A	D—H···A
C6′A—H6′2···O12^{i}	0.99	2.56	3.349 (8)	136
C3′—H3′···O4^{ii}	0.95	2.57	3.510 (3)	170
C4′B—H4′4···O11^{iii}	0.99	2.45	3.414 (4)	164
C10—H10···O62^{iv}	0.95	2.47	3.244 (3)	138

Symmetry codes: (i) $-x+1, -y+2, -z+1$; (ii) $x-1, y-1, z$; (iii) $-x+1, -y+1, -z+1$; (iv) $-x+2, -y+2, -z+1$.

The structure of **2** was established using spectroscopic (MS and NMR) data, while its stereochemistry was determined based mainly on the synthetic pathway and implied by the X-ray analysis. The thiazolic compound **2** is finally identified as dimethyl 2-((2*Z*,5*Z*)-5-(2-methoxy-2-oxoethylidene)-2-{(*E*)-[2-methyl-5-(prop-1-en-2-yl)cyclohex-2-enylidene]hydrazinylidene}-4-oxothiazolidin-3-yl)fumarate.

2. Structural commentary

The title molecule is built up from an oxothiazolidine ring tetrasubstituted by a methoxy-oxoethylidene, a fumarate, an oxygen and a cyclohexylidene-hydrazone (Fig. 1). As expected, the thiazolidine ring and all the atoms attached to it (plane A = S1/C2/N3/C4/C5/N2/C7/O4/C10) are roughly coplanar with the largest deviation from the mean plane being 0.085 (2) Å for C10. The butadiene fragment (C1′/C2′/C3′/C4′A/C4′B) of the cyclohexylidene ring is twisted slightly with respect to this plane, making a dihedral angle of 8.3 (2)°. The methoxycarbonyl group (C11/O11/O12/C12) is also twisted slightly with respect to plane A, with a dihedral angle of 8.2 (2)°. The methoxycarbonyl groups (C6/O61/O62/C14 and C9/O91/O92/C13) of the fumarate group make dihedral angles

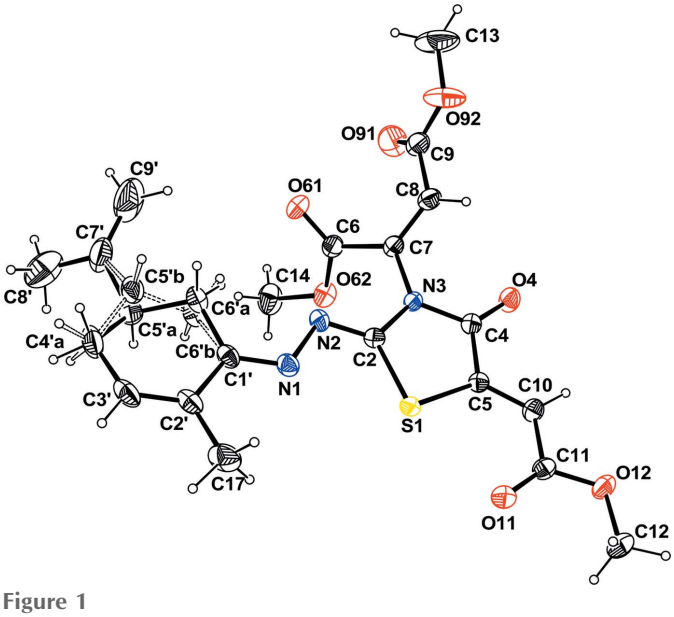


Figure 1
The molecular view of the title compound with the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level. H atoms are represented as small circle of arbitrary radii. The disordered part is shown with dashed lines.

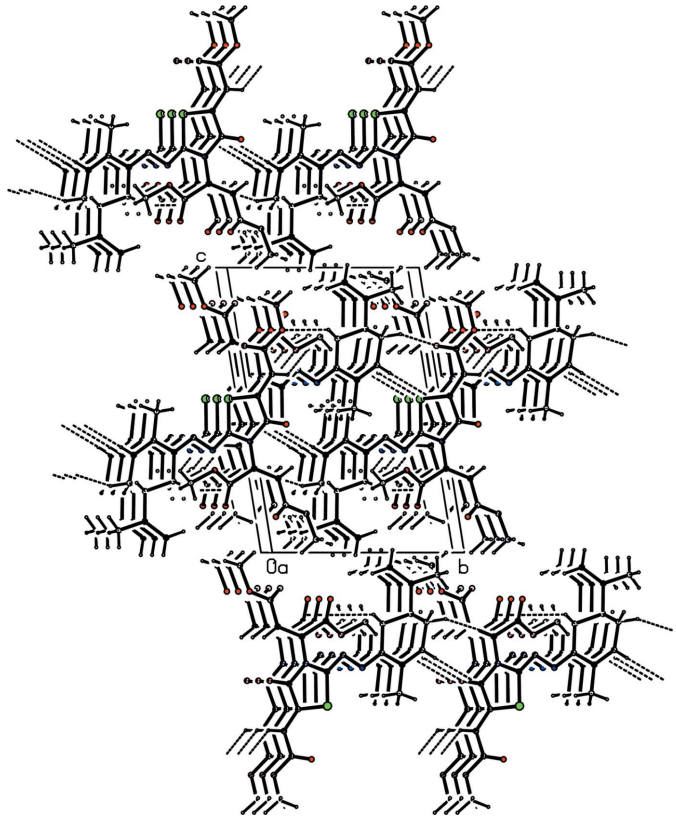


Figure 2
A packing view showing the formation of layers parallel to the (001) plane.

of 70.06 (7) and 75.59 (9)°, respectively, with the thiazolidine ring.

The most striking feature of this structure is the conformational statistical disorder which affects the cyclohexylidene ring: atoms C6′ and C5′ are split over two positions, each of half occupancy, with respect to the mean plane of the butadiene (C1′–C4′) fragment (Fig.1). Such disorder inverts the configuration at C5 (***R*** C5′A and ***S*** C5′B) and so the crystal might be considered as a racemate. Could the crystal be considered as a co-crystal built up from the combination of ***R*** and ***S*** configurations? It is difficult to answer this question.

3. Supramolecular features

In the crystal, there are C—H···O weak hydrogen-bonding interactions (Table 1) which link the molecules, building a two-dimensional network parallel to the (001) plane, as shown in Fig. 2.

4. Database survey

A search of the Cambridge Structural Database (CSD, Version 5.37, update November 2015; Groom *et al.*, 2016) using a thiazolidine ring substituted by a hydrazone linked to a cyclohexyl ring as the main skeleton, revealed the presence of six structures.

Scheme 2

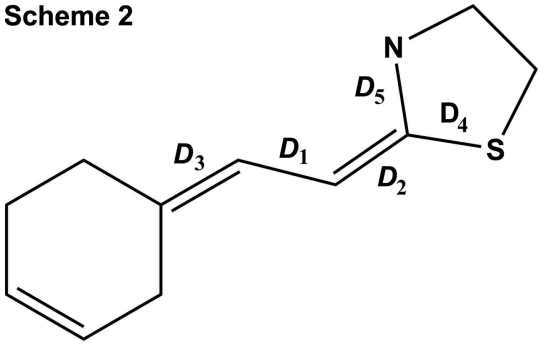


Table 2
Comparison of main bond lengths and C═N—N═C torsion angles (Å, °) in the title compound and related structures.

For a definition of the distances *D*, see Scheme 2.

Refcode	*D*1	*D*2	*D*3	*D*4	*D*5	Torsion
MUDRIO	1.406	1.277	1.287	1.769	1.386	179.0
FOTQEM	1.417	1.269	1.292	1.756	1.380	173.8
MIZJUC	1.407	1.281	1.291	1.761	1.392	179.4
ROMXUN	1.414	1.278	1.278	1.749	1.367	−177.3
WISTAV	1.429	1.256	1.278	1.753	1.413	−177.6
WISTAV	1.412	1.290	1.288	1.758	1.354	177.2
WURVAI	1.410	1.279	1.279	1.768	1.364	174.9
This study	1.405 (3)	1.274 (3)	1.286 (4)	1.756 (3)	1.398 (3)	−168.9 (2)

Reference: MUDRIO: Mohamed *et al.* (2015); FOTQEM: Gautam & Chaudhary (2015); MIZJUC: Mague *et al.* (2014); ROMXUN: Ramachandran *et al.* (2009); WISTAV: Gupta & Chaudhary (2013); WURVAI: Gautam *et al.* (2013).

A comparison of the main C—N, N—N, C—S distances in the title compound and the structures extracted from the CSD shows good correlation: within the C═N—N═C fragment, the double bonds are located on the CN, the N—N distance is that of a single bond corresponding to a hydrazono group. The C═N—N═C torsion angles (Table 2) indicate that in each case the four atoms are nearly planar.

5. Synthesis and crystallization

A solution of (1*R*)-thiosemicarbazone carvone **1** and dimethyl acetylenedicarboxylate (1.25 eq) in anhydrous MeCN (50 mL), was heated under reflux for 30 min. After the completion of the reaction (the progress of the reaction was monitored by TLC), the solvent was evaporated to dryness. The crude product was purified by silica gel chromatography (230–400 mesh) using hexane/ethyl acetate (95:5) as eluent. The pure thiazolic product **2** was obtained in 65% yield. Slow evaporation from an ethanolic solution of the title compound gave crystals of **2** suitable for crystallographic analysis.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. The disorder was been refined using the tools available in *SHELXL2014*. All H atoms were initially located in a difference Fourier map but were placed in geometrically idealized positions and constrained to ride on their parent atoms with C—H = 0.95–1.0 Å and O—H = 0.84 Å, with U_{iso}(H) = 1.5U_{eq}(C) for methyl H atoms and 1.2U_{eq}(C,O) for all other H atoms.

Table 3
Experimental details.

Crystal data	
Chemical formula	$C_{22}H_{25}N_3O_7S$
M_r	475.51
Crystal system, space group	Triclinic, $P\overline{1}$
Temperature (K)	173
a, *b*, *c* (Å)	8.2468 (3), 9.8783 (4), 15.1039 (6)
α, β, γ (°)	96.144 (2), 105.172 (2), 95.750 (2)
V (Å^3)	1170.14 (8)
Z	2
Radiation type	Mo *K*α
μ (mm^{-1})	0.19
Crystal size (mm)	0.37 × 0.25 × 0.03
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan (*SADABS*; Sheldrick, 2008)
T_{min}, T_{max}	0.732, 1.0
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	34166, 4778, 4085
R_{int}	0.041
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.055, 0.123, 1.22
No. of reflections	4778
No. of parameters	315
No. of restraints	3
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.30, −0.26

Computer programs: *APEX2* and *SAINT* (Bruker, 2014), *SHELXT2013* (Sheldrick, 2015*a*), *SHELXL2014* (Sheldrick, 2015*b*), *ORTEPIII* (Burnett & Johnson, 1996), *ORTEP-3 for Windows* (Farrugia, 2012), *Mercury* (Macrae *et al.*, 2008) and *PLATON* (Spek, 2009).

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supporting information

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Crystal structure of dimethyl 2-((2*Z*,5*Z*)-5-(2-methoxy-2-oxoethylidene)-2-{(*E*)-[2-methyl-5-(prop-1-en-2-yl)cyclohex-2-enylidene]hydrazinylidene}-4-oxothiazolidin-3-yl)fumarate

Abdellah N'ait Ousidi, My Youssef Ait Itto, Aziz Auhmani, Abdelkhalek Riahi, Abdelwahed Auhmani and Jean-Claude Daran

Computing details

Data collection: *APEX2* (Bruker, 2014); cell refinement: *SAINT* (Bruker, 2014); data reduction: *SAINT* (Bruker, 2014); program(s) used to solve structure: SHELXT2013 (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015b); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996), *ORTEP-3 for Windows* (Farrugia, 2012), *Mercury* (Macrae *et al.*, 2008) and *PLATON* (Spek, 2009); software used to prepare material for publication: *SHELXL2014* (Sheldrick, 2015b).

Dimethyl 2-((2*Z*,5*Z*)-5-(2-methoxy-2-oxoethylidene)-2-{(*E*)-[2-methyl-5-(prop-1-en-2-yl)cyclohex-2-enylidene]hydrazinylidene}-4-oxothiazolidin-3-yl)fumarate

Crystal data

$C_{22}H_{25}N_3O_7S$
$M_r = 475.51$
Triclinic, $P\overline{1}$
$a = 8.2468$ (3) Å
$b = 9.8783$ (4) Å
$c = 15.1039$ (6) Å
$\alpha = 96.144$ (2)°
$\beta = 105.172$ (2)°
$\gamma = 95.750$ (2)°
$V = 1170.14$ (8) Å^3
$Z = 2$
$F(000) = 500$
$D_x = 1.350$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 8618 reflections
$\theta = 2.4$–26.8°
$\mu = 0.19$ mm^{-1}
$T = 173$ K
Flattened, yellow
0.37 × 0.25 × 0.03 mm

Data collection

Bruker APEXII CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
φ and ω scans
Absorption correction: multi-scan (SADABS; Sheldrick, 2008)
$T_{min} = 0.732$, $T_{max} = 1.0$
34166 measured reflections
4778 independent reflections
4085 reflections with $I > 2\sigma(I)$
$R_{int} = 0.041$
$\theta_{max} = 26.4°$, $\theta_{min} = 2.6°$
$h = -10 \rightarrow 10$
$k = -12 \rightarrow 12$
$l = -18 \rightarrow 18$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.055$
$wR(F^2) = 0.123$
$S = 1.22$
4778 reflections
315 parameters
3 restraints

Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0088P)^2 + 2.0702P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.30$ e Å^{-3}
$\Delta\rho_{min} = -0.26$ e Å^{-3}

Special details

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.

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

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
S1	0.62041 (8)	0.86199 (7)	0.53866 (5)	0.02031 (15)	
N1	0.3971 (3)	0.6620 (2)	0.40411 (16)	0.0238 (5)	
N2	0.4884 (3)	0.7458 (2)	0.35923 (16)	0.0219 (5)	
N3	0.6949 (3)	0.9353 (2)	0.38976 (15)	0.0197 (5)	
O4	0.8958 (2)	1.1256 (2)	0.45018 (13)	0.0279 (5)	
O11	0.7109 (3)	0.9837 (2)	0.72559 (14)	0.0310 (5)	
O12	0.8836 (3)	1.1828 (2)	0.78060 (13)	0.0298 (5)	
O61	0.5937 (3)	0.7601 (2)	0.16332 (14)	0.0376 (5)	
O62	0.7897 (2)	0.7213 (2)	0.28911 (14)	0.0282 (4)	
O91	0.7901 (4)	1.0015 (3)	0.12561 (17)	0.0515 (7)	
O92	0.6342 (3)	1.1721 (3)	0.13646 (17)	0.0538 (7)	
C2	0.5920 (3)	0.8376 (3)	0.41840 (18)	0.0197 (5)	
C4	0.7978 (3)	1.0332 (3)	0.46061 (18)	0.0199 (5)	
C5	0.7660 (3)	1.0086 (3)	0.55003 (18)	0.0191 (5)	
C1′	0.3108 (3)	0.5531 (3)	0.3521 (2)	0.0234 (6)	
C6′A	0.2869 (12)	0.5260 (9)	0.2500 (10)	0.0287 (17)	0.5
H6′1	0.3901	0.5660	0.2354	0.034*	0.5
H6′2	0.1910	0.5715	0.2179	0.034*	0.5
C5′A	0.2517 (8)	0.3731 (6)	0.2149 (4)	0.0268 (13)	0.5
H5′A	0.3538	0.3305	0.2444	0.032*	0.5
C4′A	0.1024 (4)	0.3074 (3)	0.2435 (3)	0.0405 (8)	0.5
H4′1	−0.0037	0.3307	0.2033	0.049*	0.5
H4′2	0.0986	0.2063	0.2335	0.049*	0.5
C6′B	0.3359 (11)	0.4961 (9)	0.2590 (10)	0.0287 (17)	0.5
H6′3	0.3707	0.5733	0.2283	0.034*	0.5
H6′4	0.4280	0.4377	0.2698	0.034*	0.5
C5′B	0.1756 (9)	0.4123 (7)	0.1957 (5)	0.0335 (15)	0.5
H5′B	0.0900	0.4759	0.1758	0.040*	0.5
C4′B	0.1024 (4)	0.3074 (3)	0.2435 (3)	0.0405 (8)	0.5
H4′3	−0.0178	0.2782	0.2087	0.049*	0.5

H4′4	0.1626	0.2259	0.2407	0.049*	0.5
C3′	0.1105 (4)	0.3520 (3)	0.3419 (2)	0.0345 (7)	
H3′	0.0414	0.2975	0.3696	0.041*	
C2′	0.2076 (3)	0.4630 (3)	0.3939 (2)	0.0268 (6)	
C17	0.2189 (4)	0.5009 (4)	0.4944 (2)	0.0407 (8)	
H17A	0.1542	0.4280	0.5151	0.061*	
H17B	0.1721	0.5872	0.5028	0.061*	
H17C	0.3378	0.5124	0.5310	0.061*	
C6	0.6828 (3)	0.7956 (3)	0.24011 (19)	0.0250 (6)	
C7	0.6900 (3)	0.9341 (3)	0.29482 (18)	0.0212 (5)	
C8	0.6931 (3)	1.0514 (3)	0.26006 (19)	0.0265 (6)	
H8	0.6827	1.1316	0.2978	0.032*	
C9	0.7115 (4)	1.0664 (3)	0.1666 (2)	0.0322 (7)	
C10	0.8410 (3)	1.0963 (3)	0.62646 (18)	0.0228 (6)	
H10	0.9203	1.1714	0.6238	0.027*	
C11	0.8037 (3)	1.0792 (3)	0.71487 (19)	0.0237 (6)	
C12	0.8491 (5)	1.1760 (3)	0.8692 (2)	0.0388 (8)	
H12A	0.7274	1.1754	0.8618	0.058*	
H12B	0.9120	1.2561	0.9131	0.058*	
H12C	0.8846	1.0918	0.8927	0.058*	
C13	0.6425 (6)	1.2005 (5)	0.0456 (3)	0.0715 (14)	
H13A	0.7613	1.2236	0.0463	0.107*	
H13B	0.5807	1.2779	0.0291	0.107*	
H13C	0.5913	1.1191	0.0000	0.107*	
C14	0.7916 (4)	0.5857 (3)	0.2438 (3)	0.0421 (8)	
H14A	0.6766	0.5354	0.2253	0.063*	
H14B	0.8672	0.5364	0.2866	0.063*	
H14C	0.8322	0.5930	0.1889	0.063*	
C7′	0.2228 (5)	0.3479 (4)	0.1088 (3)	0.0488 (9)	
C9′	0.2088 (5)	0.2048 (5)	0.0776 (3)	0.0663 (12)	
H9′1	0.2373	0.1919	0.0185	0.100*	
H9′2	0.0924	0.1619	0.0693	0.100*	
H9′3	0.2871	0.1621	0.1237	0.100*	
C8′	0.2471 (7)	0.4446 (5)	0.0520 (3)	0.0794 (16)	
H8′1	0.2547	0.4159	−0.0087	0.095*	
H8′2	0.2562	0.5397	0.0737	0.095*	

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0217 (3)	0.0199 (3)	0.0195 (3)	0.0015 (2)	0.0057 (3)	0.0047 (2)
N1	0.0222 (12)	0.0232 (12)	0.0266 (12)	−0.0003 (9)	0.0081 (10)	0.0056 (10)
N2	0.0214 (11)	0.0193 (11)	0.0244 (12)	−0.0011 (9)	0.0067 (9)	0.0033 (9)
N3	0.0215 (11)	0.0198 (11)	0.0166 (11)	−0.0013 (9)	0.0049 (9)	0.0016 (9)
O4	0.0274 (11)	0.0287 (11)	0.0256 (11)	−0.0073 (8)	0.0094 (8)	−0.0002 (8)
O11	0.0389 (12)	0.0293 (11)	0.0240 (11)	−0.0007 (9)	0.0086 (9)	0.0054 (9)
O12	0.0362 (12)	0.0320 (11)	0.0185 (10)	0.0004 (9)	0.0066 (8)	−0.0025 (8)
O61	0.0493 (14)	0.0339 (12)	0.0207 (11)	−0.0022 (10)	−0.0007 (10)	−0.0019 (9)

O62	0.0235 (10)	0.0307 (11)	0.0292 (11)	0.0061 (8)	0.0064 (8)	−0.0015 (9)
O91	0.0797 (19)	0.0446 (15)	0.0402 (14)	0.0044 (13)	0.0363 (14)	0.0033 (11)
O92	0.0513 (15)	0.082 (2)	0.0399 (14)	0.0191 (14)	0.0174 (12)	0.0396 (14)
C2	0.0187 (13)	0.0215 (13)	0.0199 (13)	0.0032 (10)	0.0064 (10)	0.0040 (11)
C4	0.0173 (12)	0.0207 (13)	0.0214 (13)	0.0040 (10)	0.0048 (10)	0.0021 (11)
C5	0.0165 (12)	0.0206 (13)	0.0201 (13)	0.0030 (10)	0.0044 (10)	0.0032 (10)
C1′	0.0186 (13)	0.0208 (13)	0.0320 (15)	0.0024 (10)	0.0072 (11)	0.0080 (12)
C6′A	0.032 (5)	0.020 (4)	0.035 (3)	−0.001 (3)	0.012 (4)	0.003 (3)
C5′A	0.023 (3)	0.027 (3)	0.028 (3)	0.005 (3)	0.001 (3)	0.005 (3)
C4′A	0.0361 (18)	0.0239 (16)	0.054 (2)	−0.0081 (13)	0.0055 (16)	0.0035 (15)
C6′B	0.032 (5)	0.020 (4)	0.035 (3)	−0.001 (3)	0.012 (4)	0.003 (3)
C5′B	0.026 (4)	0.026 (3)	0.042 (4)	−0.001 (3)	−0.003 (3)	0.006 (3)
C4′B	0.0361 (18)	0.0239 (16)	0.054 (2)	−0.0081 (13)	0.0055 (16)	0.0035 (15)
C3′	0.0262 (15)	0.0279 (16)	0.050 (2)	−0.0018 (12)	0.0095 (14)	0.0179 (14)
C2′	0.0201 (13)	0.0237 (14)	0.0392 (17)	0.0035 (11)	0.0089 (12)	0.0135 (12)
C17	0.0356 (18)	0.049 (2)	0.0427 (19)	−0.0017 (15)	0.0182 (15)	0.0174 (16)
C6	0.0251 (14)	0.0271 (15)	0.0225 (14)	−0.0019 (11)	0.0086 (11)	0.0020 (11)
C7	0.0192 (13)	0.0246 (14)	0.0192 (13)	−0.0010 (10)	0.0062 (10)	0.0015 (11)
C8	0.0262 (14)	0.0322 (16)	0.0200 (14)	−0.0001 (12)	0.0057 (11)	0.0034 (12)
C9	0.0319 (16)	0.0365 (17)	0.0245 (15)	−0.0100 (13)	0.0062 (13)	0.0052 (13)
C10	0.0193 (13)	0.0249 (14)	0.0229 (14)	0.0010 (11)	0.0052 (11)	0.0009 (11)
C11	0.0207 (13)	0.0282 (15)	0.0207 (14)	0.0047 (11)	0.0029 (11)	0.0029 (11)
C12	0.056 (2)	0.0400 (18)	0.0198 (15)	0.0021 (16)	0.0129 (14)	−0.0015 (13)
C13	0.072 (3)	0.106 (4)	0.042 (2)	0.003 (3)	0.013 (2)	0.047 (2)
C14	0.0433 (19)	0.0330 (18)	0.049 (2)	0.0118 (15)	0.0124 (16)	−0.0060 (15)
C7′	0.055 (2)	0.043 (2)	0.039 (2)	−0.0142 (17)	0.0121 (17)	−0.0122 (16)
C9′	0.051 (2)	0.088 (3)	0.052 (3)	0.021 (2)	0.001 (2)	−0.006 (2)
C8′	0.108 (4)	0.073 (3)	0.050 (3)	−0.021 (3)	0.034 (3)	−0.027 (2)

Geometric parameters (Å, º)

S1—C5	1.749 (3)	C5′B—C4′B	1.491 (7)
S1—C2	1.756 (3)	C5′B—C7′	1.555 (8)
N1—C1′	1.286 (4)	C5′B—H5′B	1.0000
N1—N2	1.405 (3)	C4′B—C3′	1.486 (5)
N2—C2	1.274 (3)	C4′B—H4′3	0.9900
N3—C4	1.393 (3)	C4′B—H4′4	0.9900
N3—C2	1.398 (3)	C3′—C2′	1.330 (4)
N3—C7	1.423 (3)	C3′—H3′	0.9500
O4—C4	1.208 (3)	C2′—C17	1.500 (4)
O11—C11	1.206 (3)	C17—H17A	0.9800
O12—C11	1.331 (3)	C17—H17B	0.9800
O12—C12	1.446 (3)	C17—H17C	0.9800
O61—C6	1.193 (3)	C6—C7	1.508 (4)
O62—C6	1.329 (3)	C7—C8	1.322 (4)
O62—C14	1.441 (4)	C8—C9	1.480 (4)
O91—C9	1.193 (4)	C8—H8	0.9500
O92—C9	1.337 (4)	C10—C11	1.469 (4)

O92—C13	1.447 (4)	C10—H10	0.9500
C4—C5	1.481 (4)	C12—H12A	0.9800
C5—C10	1.331 (4)	C12—H12B	0.9800
C1′—C2′	1.472 (4)	C12—H12C	0.9800
C1′—C6′A	1.492 (14)	C13—H13A	0.9800
C1′—C6′B	1.531 (14)	C13—H13B	0.9800
C6′A—C5′A	1.519 (9)	C13—H13C	0.9800
C6′A—H6′1	0.9900	C14—H14A	0.9800
C6′A—H6′2	0.9900	C14—H14B	0.9800
C5′A—C4′A	1.517 (7)	C14—H14C	0.9800
C5′A—C7′	1.547 (7)	C7′—C8′	1.383 (6)
C5′A—H5′A	1.0000	C7′—C9′	1.425 (6)
C4′A—C3′	1.486 (5)	C9′—H9′1	0.9800
C4′A—H4′1	0.9900	C9′—H9′2	0.9800
C4′A—H4′2	0.9900	C9′—H9′3	0.9800
C6′B—C5′B	1.516 (10)	C8′—H8′1	0.9500
C6′B—H6′3	0.9900	C8′—H8′2	0.9500
C6′B—H6′4	0.9900		

C5—S1—C2	90.20 (12)	C2′—C3′—H3′	117.7
C1′—N1—N2	113.9 (2)	C4′A—C3′—H3′	117.7
C2—N2—N1	110.0 (2)	C3′—C2′—C1′	119.1 (3)
C4—N3—C2	114.9 (2)	C3′—C2′—C17	123.1 (3)
C4—N3—C7	123.6 (2)	C1′—C2′—C17	117.8 (3)
C2—N3—C7	121.6 (2)	C2′—C17—H17A	109.5
C11—O12—C12	114.8 (2)	C2′—C17—H17B	109.5
C6—O62—C14	115.3 (2)	H17A—C17—H17B	109.5
C9—O92—C13	115.4 (3)	C2′—C17—H17C	109.5
N2—C2—N3	120.4 (2)	H17A—C17—H17C	109.5
N2—C2—S1	126.7 (2)	H17B—C17—H17C	109.5
N3—C2—S1	112.80 (18)	O61—C6—O62	125.7 (3)
O4—C4—N3	125.0 (2)	O61—C6—C7	123.8 (3)
O4—C4—C5	125.3 (2)	O62—C6—C7	110.5 (2)
N3—C4—C5	109.7 (2)	C8—C7—N3	119.4 (2)
C10—C5—C4	120.1 (2)	C8—C7—C6	124.1 (2)
C10—C5—S1	127.5 (2)	N3—C7—C6	116.4 (2)
C4—C5—S1	112.35 (19)	C7—C8—C9	124.6 (3)
N1—C1′—C2′	116.8 (3)	C7—C8—H8	117.7
N1—C1′—C6′A	123.9 (5)	C9—C8—H8	117.7
C2′—C1′—C6′A	118.5 (5)	O91—C9—O92	124.3 (3)
N1—C1′—C6′B	124.6 (4)	O91—C9—C8	126.6 (3)
C2′—C1′—C6′B	117.4 (5)	O92—C9—C8	108.9 (3)
C1′—C6′A—C5′A	111.6 (8)	C5—C10—C11	121.3 (2)
C1′—C6′A—H6′1	109.3	C5—C10—H10	119.3
C5′A—C6′A—H6′1	109.3	C11—C10—H10	119.3
C1′—C6′A—H6′2	109.3	O11—C11—O12	124.7 (3)
C5′A—C6′A—H6′2	109.3	O11—C11—C10	123.8 (3)
H6′1—C6′A—H6′2	108.0	O12—C11—C10	111.4 (2)

C4′A—C5′A—C6′A	110.3 (6)	O12—C12—H12A	109.5
C4′A—C5′A—C7′	111.9 (4)	O12—C12—H12B	109.5
C6′A—C5′A—C7′	110.5 (7)	H12A—C12—H12B	109.5
C4′A—C5′A—H5′A	108.0	O12—C12—H12C	109.5
C6′A—C5′A—H5′A	108.0	H12A—C12—H12C	109.5
C7′—C5′A—H5′A	108.0	H12B—C12—H12C	109.5
C3′—C4′A—C5′A	113.1 (3)	O92—C13—H13A	109.5
C3′—C4′A—H4′1	109.0	O92—C13—H13B	109.5
C5′A—C4′A—H4′1	109.0	H13A—C13—H13B	109.5
C3′—C4′A—H4′2	109.0	O92—C13—H13C	109.5
C5′A—C4′A—H4′2	109.0	H13A—C13—H13C	109.5
H4′1—C4′A—H4′2	107.8	H13B—C13—H13C	109.5
C5′B—C6′B—C1′	111.8 (8)	O62—C14—H14A	109.5
C5′B—C6′B—H6′3	109.3	O62—C14—H14B	109.5
C1′—C6′B—H6′3	109.3	H14A—C14—H14B	109.5
C5′B—C6′B—H6′4	109.3	O62—C14—H14C	109.5
C1′—C6′B—H6′4	109.3	H14A—C14—H14C	109.5
H6′3—C6′B—H6′4	107.9	H14B—C14—H14C	109.5
C4′B—C5′B—C6′B	111.7 (7)	C8′—C7′—C9′	120.9 (4)
C4′B—C5′B—C7′	112.8 (5)	C8′—C7′—C5′A	127.0 (4)
C6′B—C5′B—C7′	106.7 (7)	C9′—C7′—C5′A	110.3 (4)
C4′B—C5′B—H5′B	108.5	C8′—C7′—C5′B	111.9 (4)
C6′B—C5′B—H5′B	108.5	C9′—C7′—C5′B	125.9 (4)
C7′—C5′B—H5′B	108.5	C7′—C9′—H9′1	109.5
C3′—C4′B—C5′B	115.7 (4)	C7′—C9′—H9′2	109.5
C3′—C4′B—H4′3	108.4	H9′1—C9′—H9′2	109.5
C5′B—C4′B—H4′3	108.4	C7′—C9′—H9′3	109.5
C3′—C4′B—H4′4	108.4	H9′1—C9′—H9′3	109.5
C5′B—C4′B—H4′4	108.4	H9′2—C9′—H9′3	109.5
H4′3—C4′B—H4′4	107.4	C7′—C8′—H8′1	120.0
C2′—C3′—C4′A	124.7 (3)	C7′—C8′—H8′2	120.0
C2′—C3′—C4′B	124.7 (3)	H8′1—C8′—H8′2	120.0

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C6′*A*—H6′2···O12^{i}	0.99	2.56	3.349 (8)	136
C3′—H3′···O4^{ii}	0.95	2.57	3.510 (3)	170
C4′*B*—H4′4···O11^{iii}	0.99	2.45	3.414 (4)	164
C10—H10···O62^{iv}	0.95	2.47	3.244 (3)	138

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