

**Keywords:** crystal structure; thiazole; conformation; supramolecular structure; hydrogen bonding;  $\pi$ - $\pi$  stacking interactions

**CCDC references:** 1405409; 1405408

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# Crystal structures of two 6-(2-hydroxybenzoyl)-5*H*-thiazolo[3,2-*a*]pyrimidin-5-ones

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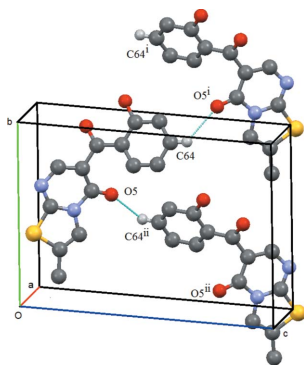
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The title compounds, 6-(2-hydroxybenzoyl)-5*H*-thiazolo[3,2-*a*]pyrimidin-5-one, C<sub>13</sub>H<sub>8</sub>N<sub>2</sub>O<sub>3</sub>S, (**1**), and 6-(2-hydroxybenzoyl)-3-methyl-5*H*-thiazolo[3,2-*a*]pyrimidin-5-one, C<sub>14</sub>H<sub>10</sub>N<sub>2</sub>O<sub>3</sub>S, (**2**), were synthesized when a chromone-3-carboxylic acid, activated with (benzotriazol-1-yloxy)tripyrrolidinylphosphonium hexafluoridophosphate (PyBOP), was reacted with a primary heteromamine. Instead of the expected amidation, the unusual title thiazolopyrimidine-5-one derivatives were obtained serendipitously and a mechanism of formation is proposed. Both compounds present an intramolecular O—H...O hydrogen bond, which generates an *S*(6) ring. The dihedral angles between the heterocyclic moiety and the 2-hydroxybenzoyl ring are 55.22 (5) and 46.83 (6)° for (**1**) and (**2**), respectively. In the crystals, the molecules are linked by weak C—H...O hydrogen bonds and  $\pi$ - $\pi$  stacking interactions.

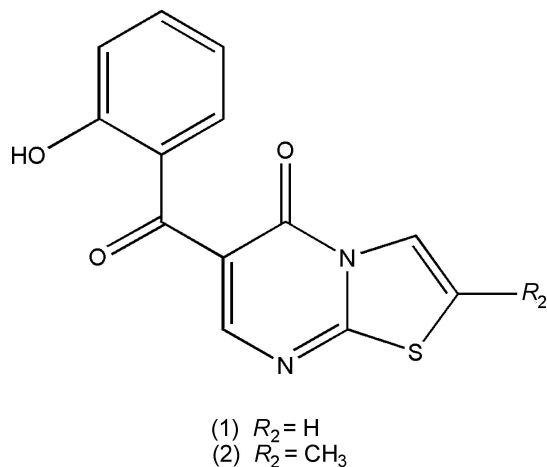
## 1. Chemical context

Although heterocycles, namely those bearing thiazole or pyrimidine motifs, are reported to show a broad spectrum of pharmacological properties such as antimicrobial, anticancer and anti-inflammatory activities (Jiang *et al.*, 2013; Mishra *et al.*, 2015; Perrone *et al.*, 2012), only a few compounds enclosing the thiazolo[3,2*a*]pyrimidine framework have been explored and screened towards the above-mentioned pharmacological activities. Even though some derivatives tested up to now have shown interesting anti-inflammatory (Bekhit *et al.*, 2003), antiviral (Abd El-Galil *et al.*, 2010) and antibacterial activities (Mulwad *et al.*, 2010) and as calcium agonists (Balkan *et al.*, 1992), the data acquired so far are insufficient to indicate the importance of the thiazolo[3,2*a*]pyrimidine motif as a positive contributor to the biological profile mentioned above. The same reflection is valid in relation to the data acquired for some thiazolo[3,2*a*]pyrimidine-5-one derivatives as 5-HT<sub>2a</sub> receptor antagonists, a putative therapeutic target for the treatment of depression, although they have structural similarity to ritanserin, a serotonin antagonist (Awadallah, 2008). In this last case, the pharmacological activity appears to be enhanced by the nature of the planar aromatic or heterocyclic ring systems, the type of spacer as well as the presence of a basic nitrogen atom.

A search made in the latest version (5.36.0; 2015) of the Cambridge Structural Database (Groom & Allen, 2014) for thiazolo[3,2*a*]pyrimidine-5-one-based structures revealed the existence of 11 compounds containing the 5*H*-thiazolo[3,2*a*]pyrimidine-5-one fragment in which the hetero ring was not fused with other cyclic rings. In order to clarify the significance

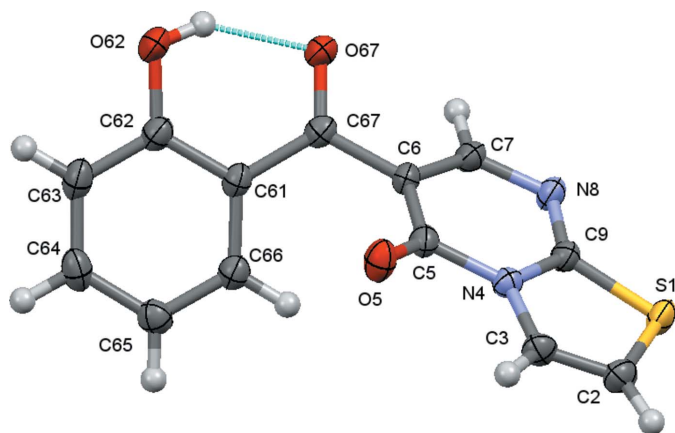


of the thiazolo[3,2-*a*]pyrimidine scaffold in medicinal chemistry, new 5*H*-thiazolo[3,2-*a*]pyrimidin-5-one derivatives were synthesized. In this work we report the structures and synthesis, by a one-pot reaction, of two derivatives 6-(2-hydroxybenzyl)-5*H*-thiazolo[3,2-*a*]pyrimidin-5-one (**1**) and 6-(2-hydroxybenzyl)-5*H*-thiazolo[3,2-*a*]pyrimidin-3-methyl-5-one (**2**), which will be screened for antimicrobial activity.

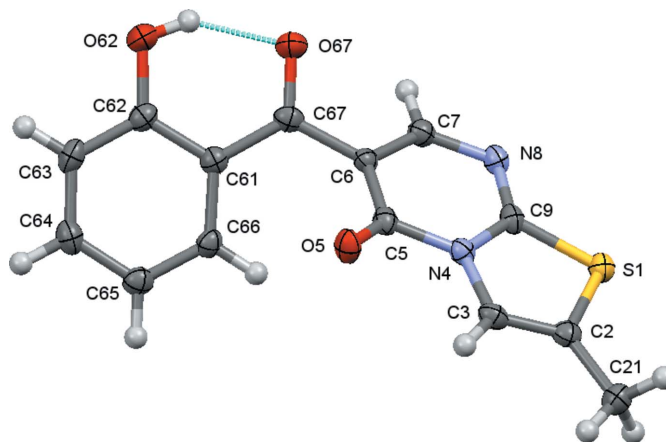


## 2. Structural commentary

The molecules of (**1**) and (**2**) are shown in Figs. 1 and 2. The structural characterization reveals that the molecules have two cyclic units, *viz.* the hydroxybenzyl and the heterocyclic 5*H*-thiazolo[3,2-*a*]pyrimidin-5-one ring separated by a carbonyl spacer, as expected. In both compounds, the carbonyl O atoms are *trans* oriented with respect to each other, contributing to the establishment of an intramolecular O—H...O hydrogen bond between the *o*-hydroxyl group of the benzene ring and the carbonyl group of the spacer (Tables 1 and 2), which generates an *S*(6) ring. Taken together, the benzene ring and hydrogen-bonded pseudo ring are roughly planar, the carbonyl oxygen atom deviates by 0.391 (3) and 0.055 (4) Å in (**1**) and (**2**), respectively from the least-square plane formed by



**Figure 1**  
 A view of the asymmetric unit of (**1**) with displacement ellipsoids drawn at the 70% probability level.



**Figure 2**  
 A view of the asymmetric unit of (**2**) with displacement ellipsoids drawn at the 70% probability level.

the benzene ring atoms. The heterocyclic rings of both compounds are also almost planar, as expected; the maximum deviation from the best plane formed by the ten atoms of the thiazolopyrimidine moiety is 0.103 (1) Å for the carbonyl oxygen atom, O5, in (**1**) and 0.129 (1) Å for the same atom in (**2**). Thus, both molecules are twisted around the C6—C67 bond that links the ring systems, which are inclined to one another by 55.22 (5) and 46.83 (6)° for (**1**) and (**2**), respectively.

## 3. Supramolecular features

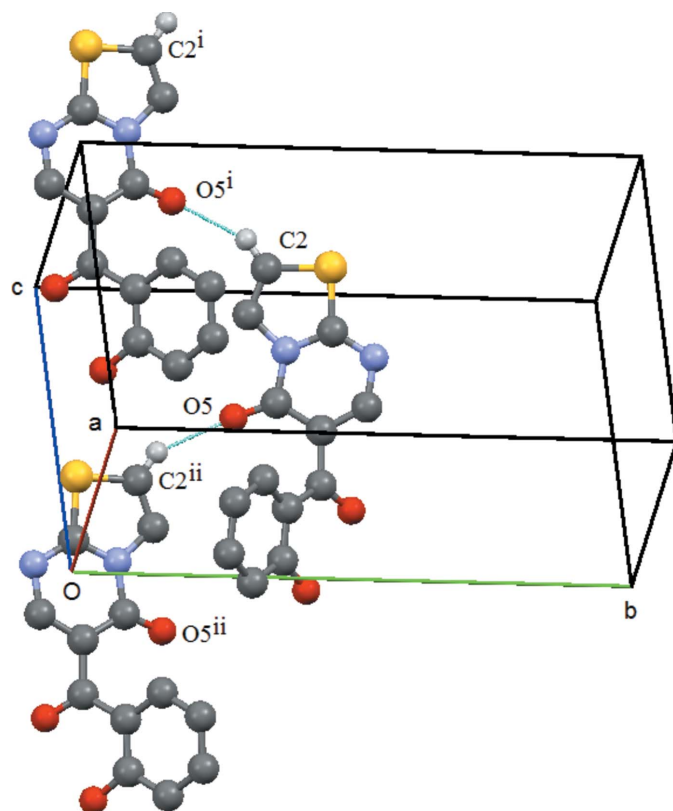
As noted above, the hydroxyl group is involved in intramolecular hydrogen bonding, which leaves it unavailable for participation in intermolecular hydrogen bonding. Thus, the molecules are linked *via* weak C—H...O interactions: in both compounds the oxygen acceptor atom is the oxo atom O5, being in (**1**) the hydrogen-bond donor atom is C2 (of the heterocyclic group) and in (**2**) the hydrogen-bond donor atom is C64 (located in the exocyclic benzene ring).

In (**1**) the molecules are linked by the C2—H2...O5 ( $x + \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2}$ ) hydrogen bond, forming a *C*(6) chain, which runs parallel to [101] and results from the action of a *c*-glide at  $(0, \frac{1}{4}, 0)$  (Table 1 and Fig. 3). The presence of the methyl group on atom C2 of the heterocyclic ring precludes the formation of a similar bond in (**2**). Thus in the supramolecular structure of this compound, the molecules are linked by a C64—H64...O5 ( $-x + 2, y + \frac{1}{2}, -z + 1$ ) hydrogen bond, forming a *C*(9) chain, which runs parallel to the *b*-axis direction and results from the action of a  $2_1$  screw axis at  $(1, y, \frac{1}{2})$  (Table 2 and Fig. 4).

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

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O62—H62A...O67	0.84	1.87	2.5906 (16)	144
C2—H2...O5 <sup>i</sup>	0.95	2.29	3.146 (2)	150

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



**Figure 3**  
Compound (1): Molecular C6 chain which runs parallel to [101]. Symmetry codes: (i)  $x + \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2}$ ; (ii)  $x - \frac{1}{2}, -y + \frac{1}{2}, z - \frac{1}{2}$ . Hydrogen atoms not involved in the hydrogen bonding are omitted.

Both molecules present aromatic  $\pi$ - $\pi$  stacking contacts. In (1) there is a close contact between centrosymmetrically related rings containing atom C5 at  $(x, y, z)$  and  $(-x + 1, -y + 1, -z + 1)$  [centroid-to-centroid distance = 3.6764 (9) Å, perpendicular distance between rings = 3.2478 (6) Å and slippage = 1.723 Å]. In (2) the molecules stack above each other along the  $a$ -axis direction with unit translation of 3.931 (2) Å [perpendicular distances between the rings (and slippages) of 3.3821 (9) (2.004), 3.3355 (9) (2.080), 3.4084 (9) (1.958) Å for the thiazole, pyrimidine and benzene rings, respectively].

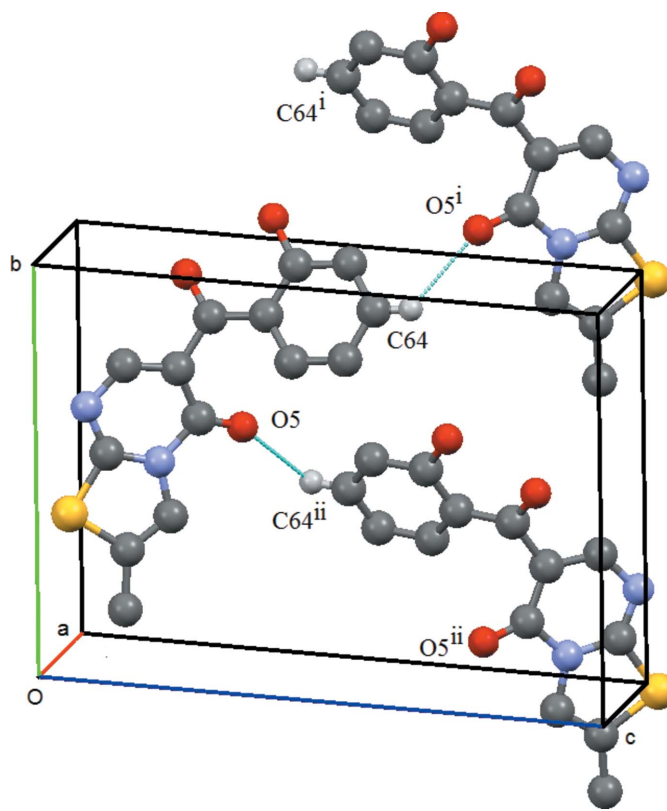
#### 4. Database survey

As said before, a search made in the latest version (5.36.0; 2015) of the Cambridge Structural Database revealed the existence of 11 deposited compounds containing the 5*H*-

**Table 2**  
Hydrogen-bond geometry (Å, °) for (2).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O62-H3 $\cdots$ O67	0.84	1.81	2.557 (2)	146
C64-H64 $\cdots$ O5 <sup>i</sup>	0.95	2.57	3.217 (3)	125

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



**Figure 4**  
Compound (2): Molecular C9 chain which runs parallel to the  $a$ -axis direction. Symmetry codes: (i)  $-x + 2, y + \frac{1}{2}, -z + 1$ ; (ii)  $-x + 2, y - \frac{1}{2}, -z + 1$ . Hydrogen atoms not involved in the hydrogen bonding are omitted.

thiazolo[3,2*a*]-pyrimidine-5-one residue. Of those, eight were 2,3-dihydro derivatives thus leaving only the compounds listed below. Fig. 5 shows representations of the compounds referred to in this work (the scaffold indicates the adopted numbering scheme for the 5*H*-thiazolo[3,2*a*]-pyrimidine-5-one residue). Compounds (1) and (2) are herein characterized and the remaining are referred to by their CSD codes. GEFTES: 7-(methylsulfanyl)-5*H*-[1,3]thiazolo[3,2-*a*]-pyrimidin-5-one (Bernhardt & Wentrup, 2012); JABRAG: 7-pentafluoroethyl-6-trifluoromethylthiazolo[3,2-*a*]pyrimidine-5-one (Chi *et al.*, 2002); NAMWEE: *N*-phenyl-6-methyl-5-oxo-5*H*-[1,3]-thiazolo[3,2-*a*]pyrimidine-2-carboxamide (Volenko *et al.*, 2004); QIBNOF: 3-ethyl-2-(4-methylthiazol-2-yl)thiazolo[3,2-*a*]pyrimidin-4-one (Troisi *et al.*, 2006); and TUFCAJ: 3-benzoyl-7-methyl-5*H*-thiazolo[3,2-*a*]pyrimidine-5-one (Elokhina *et al.*, 1996). In those compounds, the C2–C3 bond length averages 1.329 (9) Å, typical for values for a  $Csp^2-Csp^2$  bond length in thiophenes (Allen *et al.*, 1987). The average length of the C3–N4 bond at 1.397 (6) Å is slightly shorter than that for N4–C5, which is 1.418 (7) Å. The average values for the N4–C9 and C7–N8 bond lengths, 1.363 (7) and 1.357 (12) Å, respectively, are significantly shorter than the previous ones, suggesting the presence of a higher electronic density in that part of the rings. The N8–C9 average of 1.306 (9) Å is typical of a C=N bond.

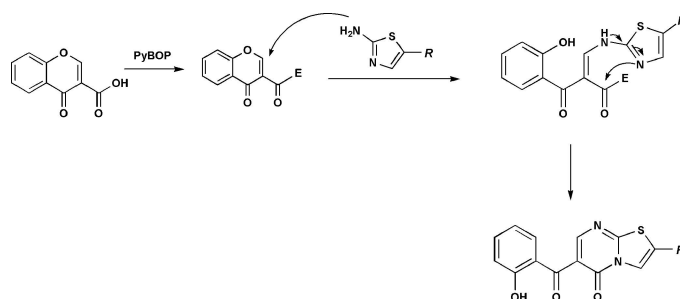
	$R_2$	$R_3$	$R_6$	$R_7$
(1)	-H	-H		-H
(2)	-CH <sub>3</sub>	-H		-H
GEFTES	-H	-H	-H	-SCH <sub>3</sub>
JABRAG	-H	-H	-CF <sub>3</sub>	-CF <sub>2</sub> CF <sub>3</sub>
NAMWEE		-H	-CH <sub>3</sub>	-H
QIBNOF	-H	-H	-CH <sub>2</sub> CH <sub>3</sub>	
TUFCAY	-H		-H	-CH <sub>3</sub>

**Figure 5**  
Representations of the compounds referred to in this work (the scaffold indicates the adopted numbering scheme for the 5*H*-thiazolo[3,2-*a*]-pyrimidine-5-one residue).

## 5. Synthesis and crystallization

Compounds **(1)** and **(2)** were synthesized in moderate/high yields by a one-pot reaction using 4-oxo-4*H*-chromene-3-carboxylic acid as the starting material. Chromone-3-carboxylic acid was initially activated with benzotriazol-1-yl-oxy-tripyrrolidinophosphonium hexafluoridophosphate (PyBOP). Then the *in situ* formed intermediate reacts with the heteroamine (stoichiometry 1:1) giving rise to 5*H*-thiazolo[3,2-*a*]-pyrimidin-5-one derivatives **(1)** (68%) and **(2)** (81%). From a mechanistic point of view, the 6-(2-hydroxybenzoyl)-5*H*-thiazolo[3,2-*a*]pyrimidin-5-one derivatives may have been obtained by a nucleophilic attack of primary heteroamine to the 2-position of the activated chromone with a subsequent opening of the pyran ring. Then, the heterocycle entities were obtained by a process involving an intramolecular reaction assisted by the nitrogen atom of the heterocycle moiety (see scheme below). Crystals were obtained by recrystallization from **(1)** in AcOEt (m.p. 454–456 K) in the form of colourless

plates and from **(2)** in CH<sub>2</sub>Cl<sub>2</sub> (m.p. 451–453 K) in the form of yellow blocks.



## 6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. H atoms were positioned geometrically and treated as riding atoms with C–H(aromatic) = 0.95 and O–H = 0.84 Å with  $U_{\text{iso}} = 1.2U_{\text{eq}}(\text{C})$  or  $1.5U_{\text{eq}}(\text{O})$ .

**Table 3**  
Experimental details.

	(1)	(2)
Crystal data		
Chemical formula	C <sub>13</sub> H <sub>8</sub> N <sub>2</sub> O <sub>3</sub> S	C <sub>14</sub> H <sub>10</sub> N <sub>2</sub> O <sub>3</sub> S
<i>M<sub>r</sub></i>	272.27	286.30
Crystal system, space group	Monoclinic, <i>P</i> <sub>2</sub> <sub>1</sub> / <i>n</i>	Monoclinic, <i>P</i> <sub>2</sub> <sub>1</sub>
Temperature (K)	100	100
<i>a</i> , <i>b</i> , <i>c</i> (Å)	7.5563 (5), 15.3187 (11), 10.1229 (7)	3.931 (2), 10.459 (6), 14.657 (8)
$\beta$ (°)	99.49 (2)	94.201 (14)
<i>V</i> (Å <sup>3</sup> )	1155.70 (15)	601.0 (6)
<i>Z</i>	4	2
Radiation type	Mo <i>K</i> $\alpha$	Mo <i>K</i> $\alpha$
$\mu$ (mm <sup>-1</sup> )	0.29	0.28
Crystal size (mm)	0.33 × 0.21 × 0.04	0.26 × 0.13 × 0.09
Data collection		
Diffractometer	Rigaku Saturn724+	Rigaku Saturn724+
Absorption correction	Multi-scan <i>CrystalClear-SM Expert</i> (Rigaku, 2012)	Multi-scan <i>CrystalClear-SM Expert</i> (Rigaku, 2012)
<i>T</i> <sub>min</sub> , <i>T</i> <sub>max</sub>	0.912, 0.989	0.931, 0.975
No. of measured, independent and observed [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )] reflections	7713, 2632, 2135	4859, 3175, 2808
<i>R</i> <sub>int</sub>	0.040	0.023
( <i>sin</i> $\theta$ / $\lambda$ ) <sub>max</sub> (Å <sup>-1</sup> )	0.649	0.729
Refinement		
<i>R</i> [ <i>F</i> <sup>2</sup> > 2 $\sigma$ ( <i>F</i> <sup>2</sup> )], <i>wR</i> ( <i>F</i> <sup>2</sup> ), <i>S</i>	0.036, 0.096, 1.02	0.031, 0.067, 1.04
No. of reflections	2632	3175
No. of parameters	172	183
No. of restraints	0	1
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained
$\Delta\rho_{\max}$ , $\Delta\rho_{\min}$ (e Å <sup>-3</sup> )	0.38, -0.22	0.35, -0.34
Absolute structure	–	Flack <i>x</i> determined using 981 quotients [[ <i>I</i> <sup>+</sup> )-( <i>I</i> <sup>-</sup> )]/[ <i>I</i> <sup>+</sup> )+( <i>I</i> <sup>-</sup> )] (Parsons <i>et al.</i> , 2013)
Absolute structure parameter	–	-0.03 (4)

Computer programs: *CrystalClear-SM Expert* (Rigaku, 2012), *SHELXS* (Sheldrick, 2008), *ShelXle* (Hübschle *et al.*, 2011), *SHELXL2014* (Sheldrick, 2015), *PLATON* (Spek, 2009), *Flipper 25* (Oszlányi & Sütő, 2004), *OSCAIL* (McArdle *et al.*, 2004) and *Mercury* (Macrae *et al.*, 2006).

## Acknowledgements

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## supporting information

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## Crystal structures of two 6-(2-hydroxybenzoyl)-5*H*-thiazolo[3,2-*a*]pyrimidin-5-ones

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### Computing details

For both compounds, data collection: *CrystalClear-SM Expert* (Rigaku, 2012); cell refinement: *CrystalClear-SM Expert* (Rigaku, 2012); data reduction: *CrystalClear-SM Expert* (Rigaku, 2012). Program(s) used to solve structure: *SHELXS* (Sheldrick, 2008) for (1); *SHELXS* (Sheldrick, 2008), *PLATON* (Spek, 2009) and *Flipper 25* (Oszlányi & Sütő, 2004) for (2). For both compounds, program(s) used to refine structure: *OSCAIL* (McArdle *et al.*, 2004), *ShelXle* (Hübschle *et al.*, 2011) and *SHELXL2014* (Sheldrick, 2015); molecular graphics: *Mercury* (Macrae *et al.*, 2006). Software used to prepare material for publication: *OSCAIL* (McArdle *et al.*, 2004) and *SHELXL2014* (Sheldrick, 2015) for (1); *OSCAIL* (McArdle *et al.*, 2004), *SHELXL2014* (Sheldrick, 2015) and *PLATON* (Spek, 2009) for (2).

### (1) 6-(2-Hydroxybenzoyl)-5*H*-thiazolo[3,2-*a*]pyrimidin-5-one

#### Crystal data

C<sub>13</sub>H<sub>8</sub>N<sub>2</sub>O<sub>3</sub>S

*M<sub>r</sub>* = 272.27

Monoclinic, *P*2<sub>1</sub>/*n*

*a* = 7.5563 (5) Å

*b* = 15.3187 (11) Å

*c* = 10.1229 (7) Å

β = 99.49 (2)°

*V* = 1155.70 (15) Å<sup>3</sup>

*Z* = 4

*F*(000) = 560

*D<sub>x</sub>* = 1.565 Mg m<sup>-3</sup>

Mo *K*α radiation, λ = 0.71075 Å

Cell parameters from 7040 reflections

θ = 2.4–27.5°

μ = 0.28 mm<sup>-1</sup>

*T* = 100 K

Plate, colourless

0.33 × 0.21 × 0.04 mm

#### Data collection

Rigaku Saturn724+ (2x2 bin mode)

diffractometer

Radiation source: Sealed Tube

Graphite Monochromator monochromator

Detector resolution: 28.5714 pixels mm<sup>-1</sup>

profile data from ω-scans

Absorption correction: multi-scan

*CrystalClear-SM Expert* (Rigaku, 2012)

*T<sub>min</sub>* = 0.912, *T<sub>max</sub>* = 0.989

7713 measured reflections

2632 independent reflections

2135 reflections with *I* > 2σ(*I*)

*R<sub>int</sub>* = 0.040

θ<sub>max</sub> = 27.5°, θ<sub>min</sub> = 3.1°

*h* = -8→9

*k* = -16→19

*l* = -13→10

#### Refinement

Refinement on *F*<sup>2</sup>

Least-squares matrix: full

*R*[*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.036

*wR*(*F*<sup>2</sup>) = 0.096

*S* = 1.02

2632 reflections

172 parameters

0 restraints

Hydrogen site location: mixed

H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0485P)^2 + 0.3293P]$$

where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.001$

$$\Delta\rho_{\max} = 0.38 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.22 \text{ e } \text{\AA}^{-3}$$

*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.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
S1	0.53044 (5)	0.47242 (3)	0.82245 (4)	0.01896 (13)
O5	0.13953 (16)	0.30924 (7)	0.48703 (11)	0.0220 (3)
O62	-0.16684 (15)	0.43565 (8)	0.04276 (11)	0.0244 (3)
H62A	-0.1549	0.4787	0.0949	0.037*
O67	-0.03352 (15)	0.51893 (7)	0.25912 (11)	0.0202 (3)
N4	0.32960 (17)	0.39593 (9)	0.62970 (12)	0.0153 (3)
N8	0.35861 (18)	0.54953 (9)	0.59756 (13)	0.0182 (3)
C2	0.4957 (2)	0.36098 (11)	0.83142 (15)	0.0200 (3)
H2	0.5482	0.3254	0.9044	0.024*
C3	0.3863 (2)	0.33073 (11)	0.72355 (15)	0.0184 (3)
H3	0.3510	0.2713	0.7121	0.022*
C5	0.2084 (2)	0.38137 (11)	0.50752 (15)	0.0167 (3)
C6	0.1834 (2)	0.45847 (10)	0.42710 (14)	0.0157 (3)
C7	0.2532 (2)	0.53721 (11)	0.47770 (15)	0.0174 (3)
H7	0.2244	0.5873	0.4232	0.021*
C9	0.3934 (2)	0.47688 (10)	0.66844 (15)	0.0159 (3)
C61	0.1006 (2)	0.39010 (10)	0.19292 (14)	0.0162 (3)
C62	-0.0209 (2)	0.38331 (11)	0.07150 (15)	0.0184 (3)
C63	0.0072 (2)	0.32092 (11)	-0.02354 (16)	0.0219 (4)
H62	-0.0774	0.3146	-0.1035	0.026*
C64	0.1571 (2)	0.26854 (11)	-0.00138 (16)	0.0217 (4)
H64	0.1752	0.2264	-0.0666	0.026*
C65	0.2832 (2)	0.27646 (11)	0.11565 (16)	0.0201 (3)
H65	0.3881	0.2413	0.1289	0.024*
C66	0.2531 (2)	0.33623 (10)	0.21201 (15)	0.0178 (3)
H66	0.3372	0.3409	0.2926	0.021*
C67	0.0738 (2)	0.45816 (10)	0.29057 (15)	0.0160 (3)

*Atomic displacement parameters ( $\text{\AA}^2$ )*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
S1	0.0213 (2)	0.0200 (2)	0.01334 (19)	-0.00121 (15)	-0.00382 (14)	0.00147 (15)
O5	0.0276 (6)	0.0188 (6)	0.0182 (6)	-0.0057 (5)	-0.0003 (5)	-0.0008 (4)
O62	0.0242 (6)	0.0272 (7)	0.0184 (6)	0.0057 (5)	-0.0068 (5)	-0.0042 (5)
O67	0.0210 (6)	0.0209 (6)	0.0167 (5)	0.0045 (5)	-0.0025 (4)	-0.0006 (4)
N4	0.0172 (6)	0.0143 (7)	0.0140 (6)	0.0011 (5)	0.0008 (5)	0.0005 (5)



N8	0.0209 (7)	0.0164 (7)	0.0151 (6)	0.0003 (5)	-0.0038 (5)	-0.0002 (5)
C2	0.0231 (8)	0.0204 (9)	0.0160 (7)	0.0034 (6)	0.0019 (6)	0.0034 (6)
C3	0.0235 (8)	0.0150 (8)	0.0166 (7)	0.0028 (6)	0.0033 (6)	0.0039 (6)
C5	0.0161 (7)	0.0188 (9)	0.0148 (7)	-0.0002 (6)	0.0015 (6)	-0.0025 (6)
C6	0.0164 (7)	0.0177 (9)	0.0122 (7)	0.0015 (6)	-0.0004 (6)	-0.0016 (6)
C7	0.0181 (7)	0.0174 (9)	0.0154 (7)	0.0019 (6)	-0.0014 (6)	0.0008 (6)
C9	0.0158 (7)	0.0156 (8)	0.0153 (7)	0.0001 (6)	-0.0007 (6)	-0.0009 (6)
C61	0.0179 (7)	0.0161 (8)	0.0136 (7)	-0.0025 (6)	0.0002 (6)	-0.0002 (6)
C62	0.0193 (7)	0.0181 (9)	0.0164 (7)	-0.0009 (6)	-0.0013 (6)	0.0013 (6)
C63	0.0283 (8)	0.0211 (9)	0.0145 (7)	-0.0042 (7)	-0.0017 (6)	-0.0004 (6)
C64	0.0328 (9)	0.0163 (9)	0.0165 (7)	-0.0029 (7)	0.0059 (7)	-0.0021 (6)
C65	0.0241 (8)	0.0163 (9)	0.0200 (8)	0.0015 (6)	0.0043 (6)	0.0006 (6)
C66	0.0196 (8)	0.0171 (9)	0.0160 (7)	-0.0015 (6)	0.0007 (6)	0.0005 (6)
C67	0.0153 (7)	0.0162 (8)	0.0158 (7)	-0.0014 (6)	0.0004 (6)	0.0016 (6)

*Geometric parameters (Å, °)*

S1—C9	1.7248 (16)	C6—C7	1.381 (2)
S1—C2	1.7318 (17)	C6—C67	1.489 (2)
O5—C5	1.225 (2)	C7—H7	0.9500
O62—C62	1.3559 (19)	C61—C66	1.404 (2)
O62—H62A	0.8405	C61—C62	1.411 (2)
O67—C67	1.2413 (19)	C61—C67	1.473 (2)
N4—C9	1.364 (2)	C62—C63	1.397 (2)
N4—C3	1.396 (2)	C63—C64	1.376 (2)
N4—C5	1.4298 (19)	C63—H62	0.9500
N8—C9	1.327 (2)	C64—C65	1.397 (2)
N8—C7	1.3503 (19)	C64—H64	0.9500
C2—C3	1.339 (2)	C65—C66	1.384 (2)
C2—H2	0.9500	C65—H65	0.9500
C3—H3	0.9500	C66—H66	0.9500
C5—C6	1.429 (2)		
C9—S1—C2	90.74 (7)	N4—C9—S1	110.78 (11)
C62—O62—H62A	109.3	C66—C61—C62	118.53 (14)
C9—N4—C3	113.61 (13)	C66—C61—C67	121.59 (14)
C9—N4—C5	122.40 (13)	C62—C61—C67	119.65 (14)
C3—N4—C5	123.91 (13)	O62—C62—C63	117.85 (14)
C9—N8—C7	113.80 (14)	O62—C62—C61	122.18 (14)
C3—C2—S1	112.14 (12)	C63—C62—C61	119.97 (15)
C3—C2—H2	123.9	C64—C63—C62	120.06 (15)
S1—C2—H2	123.9	C64—C63—H62	120.0
C2—C3—N4	112.72 (15)	C62—C63—H62	120.0
C2—C3—H3	123.6	C63—C64—C65	121.00 (15)
N4—C3—H3	123.6	C63—C64—H64	119.5
O5—C5—N4	118.75 (14)	C65—C64—H64	119.5
O5—C5—C6	129.54 (14)	C66—C65—C64	119.14 (15)
N4—C5—C6	111.69 (13)	C66—C65—H65	120.4

C7—C6—C5	120.26 (14)	C64—C65—H65	120.4
C7—C6—C67	117.84 (14)	C65—C66—C61	121.21 (15)
C5—C6—C67	121.81 (13)	C65—C66—H66	119.4
N8—C7—C6	126.02 (15)	C61—C66—H66	119.4
N8—C7—H7	117.0	O67—C67—C61	120.99 (14)
C6—C7—H7	117.0	O67—C67—C6	118.38 (14)
N8—C9—N4	125.30 (14)	C61—C67—C6	120.53 (13)
N8—C9—S1	123.91 (12)		
C9—S1—C2—C3	-0.18 (13)	C2—S1—C9—N8	-179.59 (14)
S1—C2—C3—N4	0.97 (18)	C2—S1—C9—N4	-0.67 (12)
C9—N4—C3—C2	-1.52 (19)	C66—C61—C62—O62	-176.96 (15)
C5—N4—C3—C2	-178.23 (13)	C67—C61—C62—O62	-2.4 (2)
C9—N4—C5—O5	-171.08 (14)	C66—C61—C62—C63	3.3 (2)
C3—N4—C5—O5	5.4 (2)	C67—C61—C62—C63	177.80 (14)
C9—N4—C5—C6	7.34 (19)	O62—C62—C63—C64	177.45 (15)
C3—N4—C5—C6	-176.23 (13)	C61—C62—C63—C64	-2.8 (2)
O5—C5—C6—C7	170.03 (16)	C62—C63—C64—C65	0.1 (3)
N4—C5—C6—C7	-8.2 (2)	C63—C64—C65—C66	1.9 (2)
O5—C5—C6—C67	-6.4 (3)	C64—C65—C66—C61	-1.4 (2)
N4—C5—C6—C67	175.39 (13)	C62—C61—C66—C65	-1.2 (2)
C9—N8—C7—C6	0.0 (2)	C67—C61—C66—C65	-175.63 (14)
C5—C6—C7—N8	5.1 (2)	C66—C61—C67—O67	161.58 (15)
C67—C6—C7—N8	-178.29 (14)	C62—C61—C67—O67	-12.8 (2)
C7—N8—C9—N4	-1.1 (2)	C66—C61—C67—C6	-14.7 (2)
C7—N8—C9—S1	177.67 (11)	C62—C61—C67—C6	170.93 (14)
C3—N4—C9—N8	-179.75 (14)	C7—C6—C67—O67	-40.9 (2)
C5—N4—C9—N8	-3.0 (2)	C5—C6—C67—O67	135.67 (15)
C3—N4—C9—S1	1.35 (16)	C7—C6—C67—C61	135.52 (15)
C5—N4—C9—S1	178.12 (10)	C5—C6—C67—C61	-48.0 (2)

*Hydrogen-bond geometry* (Å, °)

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O62—H62 <i>A</i> ...O67	0.84	1.87	2.5906 (16)	144
C2—H2...O5 <sup>i</sup>	0.95	2.29	3.146 (2)	150

Symmetry code: (i)  $x+1/2, -y+1/2, z+1/2$ .**(2) 6-(2-Hydroxybenzoyl)-2-methyl-5*H*-thiazolo[3,2-*a*]pyrimidin-5-one***Crystal data*C<sub>14</sub>H<sub>10</sub>N<sub>2</sub>O<sub>3</sub>S*M<sub>r</sub>* = 286.30Monoclinic, *P*2<sub>1</sub>*a* = 3.931 (2) Å*b* = 10.459 (6) Å*c* = 14.657 (8) Å $\beta$  = 94.201 (14)°*V* = 601.0 (6) Å<sup>3</sup>*Z* = 2*F*(000) = 296*D<sub>x</sub>* = 1.582 Mg m<sup>-3</sup>Mo *K*α radiation,  $\lambda$  = 0.71075 Å

Cell parameters from 1337 reflections

 $\theta$  = 2.4–31.1°

$\mu = 0.28 \text{ mm}^{-1}$   
 $T = 100 \text{ K}$

Block, yellow  
 $0.26 \times 0.13 \times 0.09 \text{ mm}$

*Data collection*

Rigaku Saturn724+ (2x2 bin mode) diffractometer  
 Radiation source: Rotating Anode  
 Confocal monochromator  
 Detector resolution:  $28.5714 \text{ pixels mm}^{-1}$   
 profile data from  $\omega$ -scans  
 Absorption correction: multi-scan  
*CrystalClear-SM Expert* (Rigaku, 2012)  
 $T_{\min} = 0.931$ ,  $T_{\max} = 0.975$

4859 measured reflections  
 3175 independent reflections  
 2808 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.023$   
 $\theta_{\max} = 31.2^\circ$ ,  $\theta_{\min} = 2.4^\circ$   
 $h = -5 \rightarrow 5$   
 $k = -14 \rightarrow 14$   
 $l = -18 \rightarrow 20$

*Refinement*

Refinement on  $F^2$   
 Least-squares matrix: full  
 $R[F^2 > 2\sigma(F^2)] = 0.031$   
 $wR(F^2) = 0.067$   
 $S = 1.04$   
 3175 reflections  
 183 parameters  
 1 restraint  
 Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained  
 $w = 1/[\sigma^2(F_o^2) + (0.0296P)^2]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} < 0.001$   
 $\Delta\rho_{\max} = 0.35 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\min} = -0.33 \text{ e } \text{\AA}^{-3}$   
 Absolute structure: Flack  $x$  determined using  
 981 quotients  $[(I^-)-(I^)]/[(I^-)+(I^)]$  (Parsons *et al.*, 2013)  
 Absolute structure parameter:  $-0.03$  (4)

*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.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
S1	0.15253 (13)	0.38511 (5)	0.04641 (4)	0.01618 (13)
O62	0.9984 (4)	1.04996 (14)	0.34842 (12)	0.0214 (4)
H3	0.9814	1.0301	0.2927	0.032*
O5	0.8745 (4)	0.55020 (15)	0.29853 (11)	0.0183 (3)
O67	0.8149 (4)	0.91654 (14)	0.20714 (11)	0.0197 (4)
N4	0.4972 (4)	0.49139 (17)	0.17956 (13)	0.0138 (4)
N8	0.2366 (5)	0.63883 (18)	0.07249 (13)	0.0159 (4)
C2	0.3438 (5)	0.2885 (2)	0.13351 (16)	0.0155 (4)
C3	0.5170 (5)	0.3595 (2)	0.19717 (15)	0.0155 (5)
H3A	0.6412	0.3241	0.2492	0.019*
C5	0.6695 (5)	0.5856 (2)	0.23699 (16)	0.0146 (4)
C6	0.5742 (5)	0.7132 (2)	0.20851 (15)	0.0129 (4)
C7	0.3746 (5)	0.7315 (2)	0.12859 (16)	0.0156 (4)
H7	0.3288	0.8175	0.1108	0.019*
C9	0.3047 (5)	0.5225 (2)	0.10207 (15)	0.0143 (4)
C21	0.3011 (6)	0.1472 (2)	0.13112 (17)	0.0196 (5)
H21A	0.4177	0.1097	0.1861	0.029*

H21B	0.3997	0.1128	0.0767	0.029*
H21C	0.0578	0.1260	0.1289	0.029*
C61	0.7116 (5)	0.8455 (2)	0.35577 (15)	0.0142 (4)
C62	0.8621 (5)	0.9562 (2)	0.39773 (16)	0.0157 (5)
C63	0.8759 (5)	0.9700 (2)	0.49229 (17)	0.0177 (5)
H63	0.9829	1.0429	0.5205	0.021*
C64	0.7340 (5)	0.8779 (2)	0.54512 (15)	0.0182 (4)
H64	0.7464	0.8878	0.6097	0.022*
C65	0.5725 (5)	0.7705 (2)	0.50554 (16)	0.0174 (5)
H65	0.4721	0.7087	0.5427	0.021*
C66	0.5602 (5)	0.7550 (2)	0.41204 (15)	0.0151 (4)
H66	0.4483	0.6824	0.3849	0.018*
C67	0.7112 (5)	0.8297 (2)	0.25681 (15)	0.0150 (4)

*Atomic displacement parameters (Å<sup>2</sup>)*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
S1	0.0175 (2)	0.0166 (3)	0.0143 (2)	−0.0011 (2)	−0.00033 (18)	−0.0012 (2)
O62	0.0274 (8)	0.0165 (8)	0.0203 (9)	−0.0060 (7)	0.0026 (7)	0.0000 (7)
O5	0.0213 (8)	0.0179 (8)	0.0148 (8)	0.0035 (7)	−0.0049 (7)	−0.0009 (7)
O67	0.0249 (8)	0.0161 (9)	0.0182 (8)	−0.0015 (6)	0.0026 (6)	0.0025 (6)
N4	0.0149 (8)	0.0143 (10)	0.0121 (9)	0.0016 (7)	0.0009 (7)	0.0007 (7)
N8	0.0173 (9)	0.0180 (10)	0.0124 (9)	0.0006 (8)	−0.0001 (7)	−0.0003 (8)
C2	0.0154 (10)	0.0164 (11)	0.0150 (11)	−0.0002 (9)	0.0032 (8)	0.0009 (9)
C3	0.0165 (9)	0.0159 (12)	0.0144 (11)	0.0029 (8)	0.0025 (8)	0.0032 (8)
C5	0.0138 (9)	0.0173 (11)	0.0131 (11)	−0.0003 (9)	0.0026 (8)	−0.0023 (9)
C6	0.0157 (9)	0.0119 (10)	0.0114 (11)	0.0004 (8)	0.0033 (8)	0.0001 (8)
C7	0.0178 (10)	0.0147 (11)	0.0144 (11)	0.0016 (9)	0.0027 (8)	0.0010 (8)
C9	0.0124 (9)	0.0179 (11)	0.0123 (11)	0.0008 (9)	0.0000 (8)	−0.0023 (9)
C21	0.0220 (11)	0.0163 (11)	0.0204 (13)	−0.0019 (10)	0.0011 (9)	−0.0017 (10)
C61	0.0138 (9)	0.0138 (11)	0.0150 (11)	0.0020 (8)	0.0008 (8)	0.0002 (8)
C62	0.0144 (9)	0.0134 (11)	0.0193 (12)	0.0009 (8)	0.0009 (8)	−0.0001 (8)
C63	0.0168 (10)	0.0145 (11)	0.0215 (12)	0.0003 (9)	−0.0018 (9)	−0.0048 (9)
C64	0.0189 (9)	0.0211 (11)	0.0144 (10)	0.0038 (12)	−0.0006 (8)	−0.0022 (11)
C65	0.0188 (10)	0.0142 (11)	0.0191 (11)	0.0017 (9)	0.0015 (9)	0.0016 (9)
C66	0.0168 (10)	0.0117 (10)	0.0166 (11)	0.0012 (8)	0.0006 (8)	−0.0012 (8)
C67	0.0148 (10)	0.0142 (10)	0.0160 (11)	0.0029 (8)	0.0011 (9)	0.0030 (9)

*Geometric parameters (Å, °)*

S1—C9	1.737 (2)	C6—C67	1.490 (3)
S1—C2	1.754 (2)	C7—H7	0.9500
O62—C62	1.352 (3)	C21—H21A	0.9800
O62—H3	0.8400	C21—H21B	0.9800
O5—C5	1.222 (3)	C21—H21C	0.9800
O67—C67	1.251 (3)	C61—C66	1.415 (3)
N4—C9	1.357 (3)	C61—C62	1.419 (3)
N4—C3	1.404 (3)	C61—C67	1.460 (3)

N4—C5	1.434 (3)	C62—C63	1.391 (3)
N8—C9	1.313 (3)	C63—C64	1.379 (3)
N8—C7	1.358 (3)	C63—H63	0.9500
C2—C3	1.339 (3)	C64—C65	1.396 (3)
C2—C21	1.487 (3)	C64—H64	0.9500
C3—H3A	0.9500	C65—C66	1.377 (3)
C5—C6	1.439 (3)	C65—H65	0.9500
C6—C7	1.375 (3)	C66—H66	0.9500
C9—S1—C2	91.17 (12)	H21A—C21—H21B	109.5
C62—O62—H3	109.5	C2—C21—H21C	109.5
C9—N4—C3	114.16 (19)	H21A—C21—H21C	109.5
C9—N4—C5	122.48 (18)	H21B—C21—H21C	109.5
C3—N4—C5	123.4 (2)	C66—C61—C62	118.2 (2)
C9—N8—C7	113.5 (2)	C66—C61—C67	122.2 (2)
C3—C2—C21	128.2 (2)	C62—C61—C67	119.57 (19)
C3—C2—S1	110.87 (17)	O62—C62—C63	118.0 (2)
C21—C2—S1	120.92 (18)	O62—C62—C61	121.9 (2)
C2—C3—N4	113.5 (2)	C63—C62—C61	120.10 (19)
C2—C3—H3A	123.3	C64—C63—C62	119.9 (2)
N4—C3—H3A	123.3	C64—C63—H63	120.0
O5—C5—N4	118.9 (2)	C62—C63—H63	120.0
O5—C5—C6	129.7 (2)	C63—C64—C65	121.3 (2)
N4—C5—C6	111.41 (19)	C63—C64—H64	119.4
C7—C6—C5	119.8 (2)	C65—C64—H64	119.4
C7—C6—C67	117.0 (2)	C66—C65—C64	119.3 (2)
C5—C6—C67	122.88 (19)	C66—C65—H65	120.3
N8—C7—C6	126.4 (2)	C64—C65—H65	120.3
N8—C7—H7	116.8	C65—C66—C61	121.1 (2)
C6—C7—H7	116.8	C65—C66—H66	119.5
N8—C9—N4	125.9 (2)	C61—C66—H66	119.5
N8—C9—S1	123.84 (17)	O67—C67—C61	121.3 (2)
N4—C9—S1	110.26 (16)	O67—C67—C6	116.06 (19)
C2—C21—H21A	109.5	C61—C67—C6	122.63 (18)
C2—C21—H21B	109.5		
C9—S1—C2—C3	-1.90 (17)	C5—N4—C9—S1	176.89 (15)
C9—S1—C2—C21	177.56 (18)	C2—S1—C9—N8	-177.19 (19)
C21—C2—C3—N4	-178.26 (19)	C2—S1—C9—N4	2.17 (15)
S1—C2—C3—N4	1.1 (2)	C66—C61—C62—O62	-176.97 (19)
C9—N4—C3—C2	0.5 (3)	C67—C61—C62—O62	1.8 (3)
C5—N4—C3—C2	-178.30 (19)	C66—C61—C62—C63	3.7 (3)
C9—N4—C5—O5	-170.18 (19)	C67—C61—C62—C63	-177.5 (2)
C3—N4—C5—O5	8.6 (3)	O62—C62—C63—C64	178.71 (19)
C9—N4—C5—C6	7.7 (3)	C61—C62—C63—C64	-1.9 (3)
C3—N4—C5—C6	-173.54 (18)	C62—C63—C64—C65	-0.6 (3)
O5—C5—C6—C7	170.2 (2)	C63—C64—C65—C66	1.2 (3)
N4—C5—C6—C7	-7.4 (3)	C64—C65—C66—C61	0.7 (3)

O5—C5—C6—C67	-3.2 (4)	C62—C61—C66—C65	-3.1 (3)
N4—C5—C6—C67	179.16 (18)	C67—C61—C66—C65	178.16 (19)
C9—N8—C7—C6	1.3 (3)	C66—C61—C67—O67	172.6 (2)
C5—C6—C7—N8	3.4 (3)	C62—C61—C67—O67	-6.1 (3)
C67—C6—C7—N8	177.25 (19)	C66—C61—C67—C6	-4.5 (3)
C7—N8—C9—N4	-1.1 (3)	C62—C61—C67—C6	176.78 (18)
C7—N8—C9—S1	178.13 (16)	C7—C6—C67—O67	-40.7 (3)
C3—N4—C9—N8	177.37 (19)	C5—C6—C67—O67	133.0 (2)
C5—N4—C9—N8	-3.8 (3)	C7—C6—C67—C61	136.6 (2)
C3—N4—C9—S1	-2.0 (2)	C5—C6—C67—C61	-49.8 (3)

*Hydrogen-bond geometry (Å, °)*

<i>D—H...A</i>	<i>D—H</i>	<i>H...A</i>	<i>D...A</i>	<i>D—H...A</i>
O62—H3...O67	0.84	1.81	2.557 (2)	146
C64—H64...O5 <sup>i</sup>	0.95	2.57	3.217 (3)	125

Symmetry code: (i)  $-x+2, y+1/2, -z+1$ .