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# Crystal structure of a new phenyl(morpholino)-methanethione derivative: 4-[(morpholin-4-yl)-carbothioyl]benzoic acid

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4-[(Morpholin-4-yl)carbothioyl]benzoic acid, C<sub>12</sub>H<sub>13</sub>NO<sub>3</sub>S, a novel phenyl(morpholino)methanethione derivative, crystallizes in the monoclinic space group *P*2<sub>1</sub>/*n*. The morpholine ring adopts a chair conformation and the carboxylic acid group is bent out slightly from the benzene ring mean plane. The molecular geometry of the carboxylic group is characterized by similar C—O bond lengths [1.266 (2) and 1.268 (2) Å] as the carboxylate H atom is disordered over two positions. This molecular arrangement leads to the formation of dimers through strong and centrosymmetric low barrier O—H···O hydrogen bonds between the carboxylic groups. In addition to these intermolecular interactions, the crystal packing consists of two different molecular sheets with an angle between their mean planes of 64.4 (2)°. The cohesion between the different layers is ensured by C—H···S and C—H···O interactions.

## 1. Chemical context

There is intense research interest in developing phenyl(morpholino)methanethione derivatives for pharmaceutical applications. They inhibit the activity of the enzymes MGL (monoacylglycerol lipase) and FAAH (fatty acid amide hydrolase) (Kapanda *et al.*, 2009; Draoui, 2009). MGL and FAAH respectively catalyse the degradation reactions of anandamide and 2-arachidonoylglycerol (2-AG) (Mechoulam *et al.*, 1995), which are endocannabinoids with beneficial effects in pathophysiological phenomena such as anxiety and pain, and neurodegenerative diseases such as Alzheimer's (Walker *et al.*, 2000; Scherma *et al.*, 2008; Zvonok *et al.*, 2008). In a continuation of our work on the synthesis of phenyl(morpholino)methanethione derivatives (Agnimonhan *et al.*, 2017), we report herein the synthesis and crystal structure analysis of a new compound, 4-[(morpholin-4-yl)carbothioyl]benzoic acid.

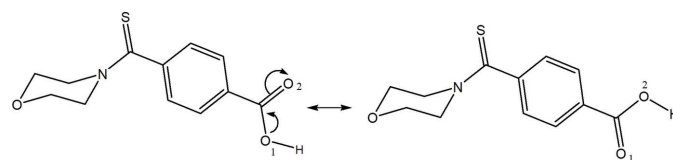
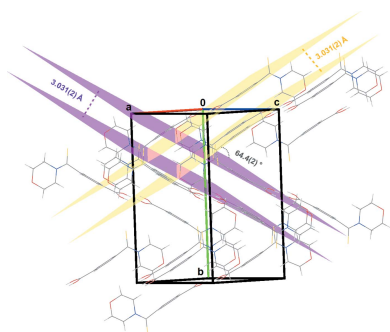


Table 1

Hydrogen-bond geometry (Å, °).

C<sub>g</sub> is the centroid of the C2–C7 ring.

D–H...A	D–H	H...A	D...A	D–H...A
C9–H9B...O1 <sup>i</sup>	0.98 (2)	2.47 (2)	3.2985 (19)	142.1 (16)
C12–H12B...S1	0.99 (3)	2.55 (2)	3.0860 (18)	113.8 (17)
O2–H1B...O1 <sup>ii</sup>	0.93 (2)	1.75 (2)	2.6661 (15)	165 (5)
O1–H1A...O2 <sup>ii</sup>	0.93 (2)	1.78 (2)	2.6661 (15)	160 (4)
C3–H3...O3 <sup>iii</sup>	0.94 (2)	2.64 (2)	3.536 (2)	158 (2)
C6–H6...S1 <sup>iv</sup>	0.89 (2)	2.996 (2)	3.8650 (14)	166 (2)
C10–H10B...C <sub>g</sub> <sup>v</sup>	1.00 (2)	2.74 (2)	3.6180 (18)	147 (2)

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

## 2. Structural commentary

The title compound (Fig. 1) crystallizes in the monoclinic space group  $P2_1/n$  with four molecules in the unit cell ( $Z = 4$ ). The hydrogen-atom coordinates were located using the high-quality residual electron density maps (Fig. 2), which also show the bonding electrons and oxygen lone pairs. The molecular structure is not planar, as shown in Fig. 1. The morpholine ring adopts a chair conformation. The torsion angle between the morpholine group and the phenyl ring around C5–C8 (C thioamide) is  $3.49 (2)^\circ$ . Such a conformation of the morpholine ring was also observed in the crystal structure of 2-methoxy-*N*-(morpholin-4-ylcarbonothioyl) benzohydrazide hemihydrate (Singh *et al.*, 2007). The carboxylic acid group is bent slightly [ $0.15 (2) \text{ \AA}$ ] out of the plane of the aromatic ring. The electron density deformation map calculated without the contribution of the carboxylic hydrogen (Fig. 2a) shows that this carboxylic H atom is split over two positions H1A and H1B, linked respectively to atoms O1 and to O2 with a refined population of 0.54 (4)/0.46 (4). This disorder is confirmed by the resulting residual map (Fig. 2b) and by the equivalent C–O1 [ $1.266 (2) \text{ \AA}$ ] and C–O2 [ $1.268 (2) \text{ \AA}$ ] bond lengths. As expected, these distances are significantly longer than classical C=O bonds [ $1.210 (8) \text{ \AA}$ ] and are shorter than conventional C–O–H [ $1.311 (2) \text{ \AA}$ ] bonds (Allen, 2002; Groom *et al.*, 2016). Given the fact that the obtained results are averaged over the time scale and space of the experiments, the distribution of the electronic density

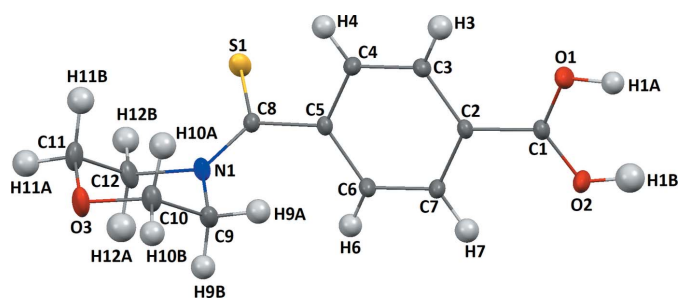


Figure 1

A view of 4-(morpholine-4-carbonothioyl) benzoic acid with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

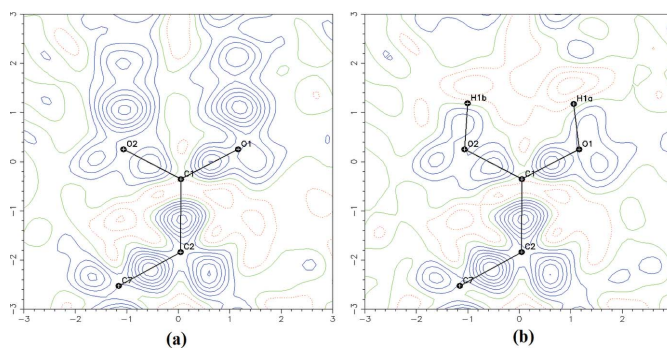


Figure 2

Residual electron density maps in the dimer COO plane calculated at the end of the independent atom refinement: (a) without the contribution of the hydrogen atom of the carboxylic group and (b) with the contribution of the hydrogen atom of the carboxylic group. The contour level is  $0.05 e \text{ \AA}^{-3}$ .

reflects the superposition of the two configurations associated with the disorder (flipping) of the hydrogen atom of the carboxylic group. Thus, the hydrogen atom is shared *via* a double-well hydrogen bond, which leads to equivalent C–O bond lengths

## 3. Supramolecular features

The crystal packing (Fig. 3) consists of two different molecular sheets. The angle between the mean planes of the two sheets is  $64.4 (2)^\circ$  and the intra-sheet distance is  $3.031 (2) \text{ \AA}$ . The building block is a centrosymmetric dimer built from strong and centrosymmetric double-well low-barrier O–H...O hydrogen bonds between two COOH groups. It is worth noting that the carboxylic groups are interconnected in a head-to-head fashion with significantly short O1...O2 interaction [ $2.666 (1) \text{ \AA}$ ]. Gilli & Gilli (2000) have documented

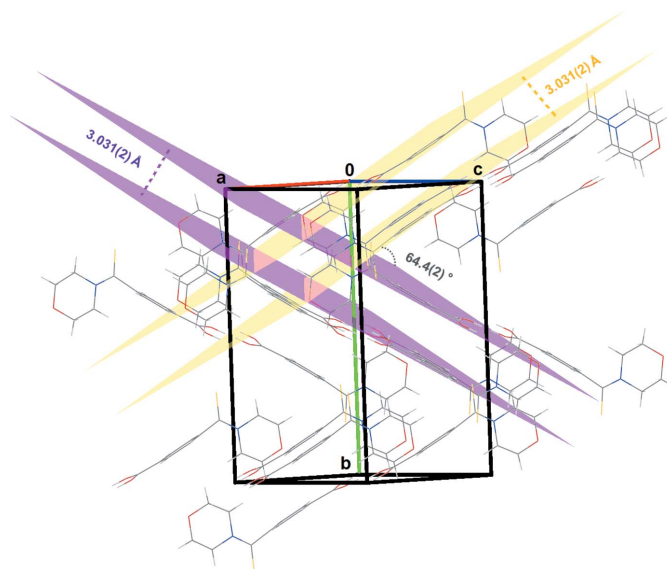
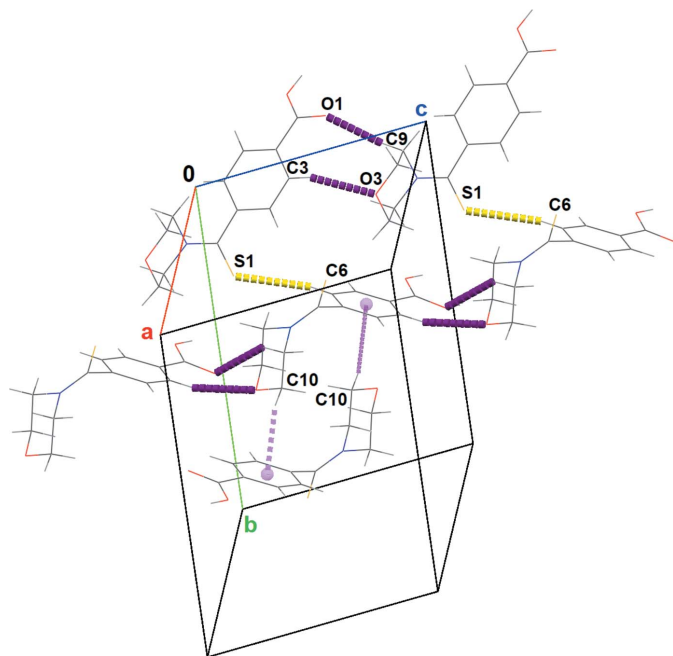


Figure 3

A packing diagram for the title compound viewed along the [101] direction, showing the arrangement of two different molecular sheets.



**Figure 4**

A projection of the three-dimensional network of intermolecular interactions (purple and yellow dotted lines) of the title compound. The C—H... $\pi$  interactions are shown with violet dashed lines.

such hydrogen bonds and similar features were also discussed by Benali-Cherif *et al.* (2014) in their work on polymorphs of *para*-amino benzoic acid. The dimers are themselves connected *via* weak intermolecular C—H...O and C—H...S interactions (Table 1, Fig. 4). Besides these short contacts, C—H... $\pi$  interactions occur between the sheets, leading to a highly linked three-dimensional network of intermolecular interactions (Fig. 4).

#### 4. Database survey

An unsubstituted analogue of the title compound has previously been reported, *viz.* morpholin-4-yl(phenyl)methanethione (Guntreddi *et al.*, 2014; Chen *et al.*, 2016). Similar structures with a planar nucleus and a chair conformation around the methanethione group have also been reported, including 1-(4-chlorothiobenzoyl)piperidine (Muthuraj *et al.*, 2007), piperidin-1-yl(pyridin-4-yl)methanethione (Ray *et al.*, 2013), ferrocen-1-yl(morpholin-4-yl)methanethione (Patra *et al.*, 2013) and (3,5-dimethyl-1*H*-pyrazo-1-yl)(morpholin-4-yl)methanethione (El-Sayed *et al.*, 2018).

#### 5. Synthesis and crystallization

All reagents along with the used solvent were obtained from Sigma–Aldrich, Prolabo and Acros Organic and used without further purification. To a mixture of 4-formylbenzoic acid (0.75 g; 5 mmol) and morpholine (0.63 ml, 7.5 mmol) in dimethylformamide (15 ml) under agitation was added montmorillonite K-10 (0.35 g) and sulfur S<sub>8</sub> (0.26 g, 8 mmol).

**Table 2**

Experimental details.

Crystal data	
Chemical formula	C <sub>12</sub> H <sub>13</sub> NO <sub>3</sub> S
<i>M<sub>r</sub></i>	251.29
Crystal system, space group	Monoclinic, <i>P</i> 2 <sub>1</sub> / <i>n</i>
Temperature (K)	293
<i>a</i> , <i>b</i> , <i>c</i> (Å)	8.3252 (1), 17.1485 (3), 9.3505 (1)
$\beta$ (°)	116.249 (1)
<i>V</i> (Å <sup>3</sup> )	1197.26 (3)
<i>Z</i>	4
Radiation type	Mo <i>K</i> $\alpha$
$\mu$ (mm <sup>-1</sup> )	0.27
Crystal size (mm)	0.15 × 0.15 × 0.08
Data collection	
Diffractometer	Bruker D8 Quest
Absorption correction	Multi-scan ( <i>SADABS</i> ; Bruker, 2019)
<i>T<sub>min</sub></i> , <i>T<sub>max</sub></i>	0.959, 0.981
No. of measured, independent and observed [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )] reflections	22827, 3664, 3317
<i>R<sub>int</sub></i>	0.024
( <i>sin</i> $\theta$ / $\lambda$ ) <sub>max</sub> (Å <sup>-1</sup> )	0.715
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>	0.048, 0.131, 1.08
No. of reflections	3664
No. of parameters	211
No. of restraints	2
H-atom treatment	All H-atom parameters refined
$\Delta\rho_{\max}$ , $\Delta\rho_{\min}$ (e Å <sup>-3</sup> )	0.55, -0.48

Computer programs: *APEX3* and *SAINT* (Bruker, 2019), *SHELXT2014* (Sheldrick, 2015a), *SHELXL2014* (Sheldrick, 2015b), *PLATON* (Spek, 2020), *Mercury* (Macrae *et al.*, 2020), *enCIFer* (Allen *et al.*, 2004) and *WinGX* (Farrugia, 2012).

The brown mixture obtained was irradiated in a microwave for 10–15 minutes at 940 W. The temperature of the reaction mixture was in the range 411–416 K. After cooling to room temperature, the mixture was poured into a solution of ethyl acetate and hydrochloric acid (0.1 *M*, 100 ml) to eliminate the excess of sulfur and amine. It was then saturated with an NH<sub>4</sub>Cl solution and finally washed with distilled water (2 × 100 ml); the organic phase obtained was dried over MgSO<sub>4</sub> before being concentrated by evaporation. Brown prismatic crystals suitable for single-crystal X-ray analysis were grown by slow evaporation from an ethanol solution at ambient temperature in the presence of air or in the freezer. The synthesized crystals were stable in air and highly soluble in polar organic solvent (*e.g.* ethyl acetate, dimethyl sulfoxide).

#### 6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. All hydrogen atoms were clearly identified in difference-Fourier maps and their atomic coordinates and isotropic displacement parameters were refined. At the end of refinement, the hydrogen atom of the carboxylic group was localized in the Fourier maps and refined accordingly by splitting its position on two sites with a refined occupancy ratio of 0.54 (4)/0.46 (4).

The quality of this room-temperature (298 K) crystal structure is also indicated by the experimental electron density

deformation maps calculated after the IAM refinement at  $0.75 \text{ \AA}^{-1}$  experimental resolution: they are of excellent quality (see Fig. 2). They show detailed features in the electron density distribution in the chemical bonds ( $0.35 \text{ e \AA}^{-3}$  for a C—C bond), electron density lone pairs and almost no noise. This surprising data quality is mostly due to the quality of the detector and to the high redundancy of the experiment [22827 collected  $I(H)$ , 3664 unique reflections, most of them (3317) having  $[I > 2\sigma(I)]$ .

### Acknowledgements

We gratefully acknowledge Professor Georges Coffi Accrombessi of the Laboratoire de Chimie Organique Physique et de Synthèse (Bénin) and Professor Jacques H. Poupaert of the Laboratoire de Chimie Thérapeutique, Ecole de Pharmacie de l'Université Catholique de Louvain, Belgium for the reagents and solvents. We also thank the X-TechLab platform at the Agence de développement de Sèmè City in Benin and the IUCr-UNESCO OpenLab for funding through the IUCr Africa fund. We also particularly thank Drs R. Durst and J. Guillin (Bruker) for the free loan of the D8 diffractometer during the Sèmè city OpenLab.

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## supporting information

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## Crystal structure of a new phenyl(morpholino)methanethione derivative: 4-[(morpholin-4-yl)carbothioyl]benzoic acid

**Finagnon Hyacinthe Agnimonhan, El-Eulmi Bendeif, Léon Ahoussi Akanni, Ahokannou Fernand Gbaguidi, Eddy Martin, Emmanuel Wenger and Claude Lecomte**

### Computing details

Data collection: *APEX3* (Bruker, 2019); cell refinement: *S SAINT* (Bruker, 2019); data reduction: *S SAINT* (Bruker, 2019), *PLATON* (Spek, 2020); program(s) used to solve structure: *SHELXT2014* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015b); molecular graphics: *Mercury* (Macrae *et al.*, 2020); software used to prepare material for publication: *enCIFer* (Allen *et al.*, 2004) and *WinGX* (Farrugia, 2012).

### 4-[(Morpholin-4-yl)carbothioyl]benzoic acid

#### Crystal data

$C_{12}H_{13}NO_3S$

$M_r = 251.29$

Monoclinic,  $P2_1/n$

$a = 8.3252$  (1) Å

$b = 17.1485$  (3) Å

$c = 9.3505$  (1) Å

$\beta = 116.249$  (1)°

$V = 1197.26$  (3) Å<sup>3</sup>

$Z = 4$

$F(000) = 528$

$D_x = 1.394$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å

Cell parameters from 22827 reflections

$\theta = 2.4$ – $30.5^\circ$

$\mu = 0.27$  mm<sup>-1</sup>

$T = 293$  K

Prism, brown

$0.15 \times 0.15 \times 0.08$  mm

#### Data collection

Bruker D8 Quest  
diffractometer

Radiation source: micro-focus sealed X-ray tube

$\omega$  scans

Absorption correction: multi-scan  
(SADABS; Bruker, 2019)

$T_{\min} = 0.959$ ,  $T_{\max} = 0.981$

22827 measured reflections

3664 independent reflections

3317 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.024$

$\theta_{\max} = 30.5^\circ$ ,  $\theta_{\min} = 2.4^\circ$

$h = -11 \rightarrow 11$

$k = -24 \rightarrow 24$

$l = -13 \rightarrow 13$

60 standard reflections every 120 min

intensity decay: none

#### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.048$

$wR(F^2) = 0.131$

$S = 1.08$

3664 reflections

211 parameters

2 restraints

Hydrogen site location: difference Fourier map

All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0661P)^2 + 0.4174P]$

where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.55$  e Å<sup>-3</sup>

$\Delta\rho_{\min} = -0.47$  e Å<sup>-3</sup>

*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 ( $\text{\AA}^2$ )*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
N1	0.44570 (18)	0.31569 (7)	0.41547 (15)	0.0357 (3)	
C9	0.4178 (2)	0.39766 (8)	0.36720 (19)	0.0375 (3)	
C10	0.5884 (2)	0.43113 (10)	0.3757 (2)	0.0453 (4)	
C11	0.6791 (3)	0.30807 (11)	0.3284 (3)	0.0539 (4)	
C12	0.5096 (3)	0.27137 (10)	0.3165 (2)	0.0470 (4)	
O3	0.65390 (19)	0.38815 (8)	0.28269 (17)	0.0541 (3)	
H7	-0.016 (3)	0.4221 (12)	0.575 (2)	0.050 (5)*	
H6	0.112 (3)	0.3489 (12)	0.444 (2)	0.046 (5)*	
H4	0.573 (3)	0.3397 (12)	0.835 (2)	0.047 (5)*	
H9A	0.378 (3)	0.4270 (12)	0.438 (2)	0.051 (5)*	
H3	0.452 (3)	0.4107 (13)	0.975 (3)	0.052 (5)*	
H9B	0.324 (3)	0.4011 (12)	0.258 (3)	0.050 (5)*	
H12B	0.532 (3)	0.2169 (15)	0.355 (3)	0.061 (6)*	
H10A	0.679 (3)	0.4269 (14)	0.494 (3)	0.062 (6)*	
H12A	0.412 (4)	0.2743 (15)	0.199 (3)	0.074 (7)*	
H11A	0.716 (3)	0.2808 (14)	0.256 (3)	0.062 (6)*	
H11B	0.783 (3)	0.3030 (14)	0.449 (3)	0.062 (6)*	
H10B	0.569 (3)	0.4855 (13)	0.333 (3)	0.053 (6)*	
H1B	-0.099 (6)	0.496 (3)	0.869 (5)	0.074 (19)*	0.54 (6)
H1A	0.147 (5)	0.509 (2)	1.062 (5)	0.045 (16)*	0.46 (6)
S1	0.47641 (7)	0.19242 (2)	0.59878 (5)	0.04786 (14)	
C2	0.20398 (17)	0.42178 (8)	0.78784 (14)	0.0292 (2)	
C5	0.35519 (17)	0.33605 (7)	0.62500 (15)	0.0283 (2)	
O1	0.21386 (16)	0.48436 (8)	1.01739 (13)	0.0468 (3)	
C1	0.11742 (19)	0.46256 (8)	0.87542 (16)	0.0333 (3)	
O2	-0.05100 (16)	0.47194 (9)	0.80599 (14)	0.0517 (3)	
C4	0.45678 (18)	0.35472 (8)	0.78541 (16)	0.0330 (3)	
C6	0.17845 (18)	0.36164 (9)	0.54576 (16)	0.0343 (3)	
C8	0.43045 (17)	0.28503 (8)	0.53941 (15)	0.0296 (2)	
C3	0.38209 (18)	0.39791 (8)	0.86649 (15)	0.0331 (3)	
C7	0.10388 (18)	0.40414 (9)	0.62725 (16)	0.0343 (3)	

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

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
N1	0.0492 (7)	0.0297 (5)	0.0396 (6)	0.0039 (5)	0.0299 (5)	-0.0014 (4)
C9	0.0458 (7)	0.0344 (7)	0.0408 (7)	0.0079 (5)	0.0269 (6)	0.0062 (5)
C10	0.0557 (9)	0.0376 (7)	0.0566 (10)	-0.0006 (6)	0.0375 (8)	-0.0012 (7)
C11	0.0636 (11)	0.0508 (9)	0.0685 (12)	0.0107 (8)	0.0486 (10)	-0.0014 (8)

C12	0.0703 (11)	0.0390 (8)	0.0488 (9)	0.0014 (7)	0.0420 (9)	-0.0097 (7)
O3	0.0700 (8)	0.0506 (7)	0.0682 (8)	0.0016 (6)	0.0547 (7)	0.0014 (6)
S1	0.0679 (3)	0.0341 (2)	0.0500 (2)	0.01608 (17)	0.0337 (2)	0.01035 (15)
C2	0.0329 (6)	0.0322 (6)	0.0277 (5)	0.0021 (4)	0.0182 (5)	-0.0003 (4)
C5	0.0311 (6)	0.0297 (6)	0.0292 (5)	0.0014 (4)	0.0181 (5)	0.0000 (4)
O1	0.0478 (6)	0.0604 (7)	0.0327 (5)	0.0117 (5)	0.0184 (5)	-0.0096 (5)
C1	0.0378 (6)	0.0367 (6)	0.0308 (6)	0.0059 (5)	0.0201 (5)	0.0003 (5)
O2	0.0395 (6)	0.0794 (9)	0.0390 (6)	0.0177 (6)	0.0200 (5)	-0.0067 (6)
C4	0.0291 (6)	0.0400 (7)	0.0301 (6)	0.0050 (5)	0.0132 (5)	-0.0006 (5)
C6	0.0309 (6)	0.0474 (7)	0.0255 (5)	0.0028 (5)	0.0134 (5)	-0.0043 (5)
C8	0.0306 (6)	0.0302 (6)	0.0312 (6)	0.0023 (4)	0.0167 (5)	-0.0016 (5)
C3	0.0332 (6)	0.0400 (7)	0.0257 (5)	0.0024 (5)	0.0128 (5)	-0.0028 (5)
C7	0.0281 (6)	0.0466 (7)	0.0299 (6)	0.0056 (5)	0.0145 (5)	-0.0019 (5)

*Geometric parameters (Å, °)*

N1—C8	1.3288 (17)	C2—C7	1.3906 (18)
N1—C9	1.4631 (18)	C2—C3	1.3938 (18)
N1—C12	1.4674 (17)	C2—C1	1.4836 (17)
C9—C10	1.501 (2)	C5—C6	1.3937 (18)
C9—H9A	1.00 (2)	C5—C4	1.3948 (18)
C9—H9B	0.98 (2)	C5—C8	1.4973 (17)
C10—O3	1.4202 (19)	O1—C1	1.2664 (17)
C10—H10A	1.03 (2)	O1—H1A	0.926 (19)
C10—H10B	1.00 (2)	C1—O2	1.2681 (18)
C11—O3	1.426 (2)	O2—H1B	0.93 (2)
C11—C12	1.503 (3)	C4—C3	1.3881 (18)
C11—H11A	0.98 (2)	C4—H4	0.91 (2)
C11—H11B	1.08 (2)	C6—C7	1.3841 (18)
C12—H12B	0.99 (3)	C6—H6	0.89 (2)
C12—H12A	1.04 (3)	C3—H3	0.94 (2)
S1—C8	1.6700 (13)	C7—H7	0.95 (2)
C8—N1—C9	125.87 (11)	C10—O3—C11	111.19 (13)
C8—N1—C12	123.12 (12)	C7—C2—C3	119.70 (11)
C9—N1—C12	110.80 (12)	C7—C2—C1	119.55 (11)
N1—C9—C10	109.51 (12)	C3—C2—C1	120.68 (11)
N1—C9—H9A	109.5 (12)	C6—C5—C4	119.66 (11)
C10—C9—H9A	110.8 (12)	C6—C5—C8	119.52 (11)
N1—C9—H9B	109.0 (13)	C4—C5—C8	120.72 (11)
C10—C9—H9B	109.6 (12)	C1—O1—H1A	112 (3)
H9A—C9—H9B	108.4 (17)	O1—C1—O2	122.96 (12)
O3—C10—C9	112.31 (14)	O1—C1—C2	118.70 (12)
O3—C10—H10A	109.0 (13)	O2—C1—C2	118.31 (12)
C9—C10—H10A	104.7 (13)	C1—O2—H1B	115 (3)
O3—C10—H10B	105.9 (13)	C3—C4—C5	120.32 (12)
C9—C10—H10B	111.0 (13)	C3—C4—H4	120.4 (13)
H10A—C10—H10B	114.1 (18)	C5—C4—H4	119.3 (13)



O3—C11—C12	111.86 (15)	C7—C6—C5	119.89 (12)
O3—C11—H11A	107.6 (14)	C7—C6—H6	120.1 (13)
C12—C11—H11A	108.8 (14)	C5—C6—H6	119.9 (13)
O3—C11—H11B	109.5 (13)	N1—C8—C5	117.32 (11)
C12—C11—H11B	109.6 (13)	N1—C8—S1	124.75 (10)
H11A—C11—H11B	109.5 (18)	C5—C8—S1	117.81 (9)
N1—C12—C11	109.05 (14)	C4—C3—C2	119.84 (12)
N1—C12—H12B	108.6 (14)	C4—C3—H3	119.8 (13)
C11—C12—H12B	110.5 (13)	C2—C3—H3	120.4 (13)
N1—C12—H12A	108.2 (15)	C6—C7—C2	120.56 (12)
C11—C12—H12A	109.0 (15)	C6—C7—H7	121.0 (13)
H12B—C12—H12A	111.5 (19)	C2—C7—H7	118.5 (13)
C8—N1—C9—C10	118.33 (16)	C8—C5—C6—C7	175.39 (13)
C12—N1—C9—C10	-56.57 (18)	C9—N1—C8—C5	8.5 (2)
N1—C9—C10—O3	55.99 (19)	C12—N1—C8—C5	-177.18 (14)
C8—N1—C12—C11	-117.94 (17)	C9—N1—C8—S1	-175.68 (12)
C9—N1—C12—C11	57.12 (19)	C12—N1—C8—S1	-1.4 (2)
O3—C11—C12—N1	-57.0 (2)	C6—C5—C8—N1	64.84 (17)
C9—C10—O3—C11	-56.2 (2)	C4—C5—C8—N1	-118.65 (15)
C12—C11—O3—C10	56.8 (2)	C6—C5—C8—S1	-111.26 (13)
C7—C2—C1—O1	-173.78 (14)	C4—C5—C8—S1	65.25 (15)
C3—C2—C1—O1	9.1 (2)	C5—C4—C3—C2	0.9 (2)
C7—C2—C1—O2	8.3 (2)	C7—C2—C3—C4	-1.9 (2)
C3—C2—C1—O2	-168.82 (14)	C1—C2—C3—C4	175.16 (13)
C6—C5—C4—C3	0.6 (2)	C5—C6—C7—C2	0.1 (2)
C8—C5—C4—C3	-175.88 (13)	C3—C2—C7—C6	1.4 (2)
C4—C5—C6—C7	-1.2 (2)	C1—C2—C7—C6	-175.72 (14)

*Hydrogen-bond geometry (Å, °)*C<sub>g</sub> is the centroid of the C2—C7 ring.

<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>
C9—H9B...O1 <sup>i</sup>	0.98 (2)	2.47 (2)	3.2985 (19)	142.1 (16)
C12—H12B...S1	0.99 (3)	2.55 (2)	3.0860 (18)	113.8 (17)
O2—H1B...O1 <sup>ii</sup>	0.93 (2)	1.75 (2)	2.6661 (15)	165 (5)
O1—H1A...O2 <sup>ii</sup>	0.93 (2)	1.78 (2)	2.6661 (15)	160 (4)
C3—H3...O3 <sup>iii</sup>	0.94 (2)	2.64 (2)	3.536 (2)	158 (2)
C6—H6...S1 <sup>iv</sup>	0.89 (2)	2.996 (2)	3.8650 (14)	166 (2)
C10—H10B...C <sub>g</sub> <sup>v</sup>	1.00 (2)	2.74 (2)	3.6180 (18)	147 (2)

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