

Crystal structure of 3-({[(morpholin-4-yl)carbonyl]sulfanyl}acetyl)phenyl benzoate

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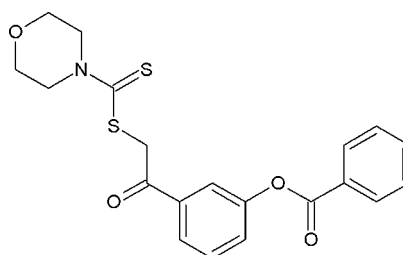
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In the title compound, C₂₀H₁₉NO₄S₂, the morpholine ring adopts the expected chair conformation. The central phenyl ring makes dihedral angles of 67.97 (4) and 7.74 (3)°, respectively, with the benzoate phenyl ring and the morpholine mean plane. In the crystal, molecules are linked by C—H···O hydrogen bonds, forming zigzag chains along the *b*-axis direction. C—H···π interactions link centrosymmetrically related molecules, reinforcing the three-dimensional structure.

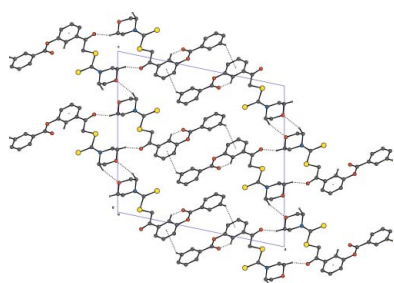
1. Chemical context

The title compound is a dithiocarbamate ester derivative of 3-(2-bromacetyl) phenyl benzoate, a key starting material used in the synthesis of phenylephrine, (*R*)-3-[1-hydroxy-2-(methylamino)ethyl] phenol, which is a selective α1-adrenergic receptor agonist used primarily as a decongestant and as an agent to dilate the pupil and to increase blood pressure. Our current research work is aimed at the synthesis of a series of 3-(2-bromacetyl) phenyl benzoate dithiocarbamate ester derivatives. Dithiocarbamate acid esters exhibit a range of biological effects, including anti-bacterial, anti-fungal and anti-oxidant activity (Hirschelman *et al.*, 2002) and inhibition of cardiac hypertrophy (Naoto *et al.* 2008). Recently, it was found that 5-oxohexyl dithiocarbamic acid methyl esters are potent phase II enzyme inducers, which could be used as cancer chemo-preventive agents (Scozzafava *et al.*, 2000).



2. Structural commentary

In the molecular structure of the title compound, the morpholine ring adopts the expected chair conformation. The phenyl ring makes dihedral angles of 67.97 (4) and 7.74 (3)° respectively with phenyl ring and the morpholine mean plane. This is also reflected in the deviation of the torsion angles C5—S1—C6—C7 = 175.32 (2) and C12—O3—C14—C15 = −178.91 (3)°. Weak intramolecular C—H···S hydrogen bonds exist within the morpholyl dithiocarbamate moiety (Table 1).



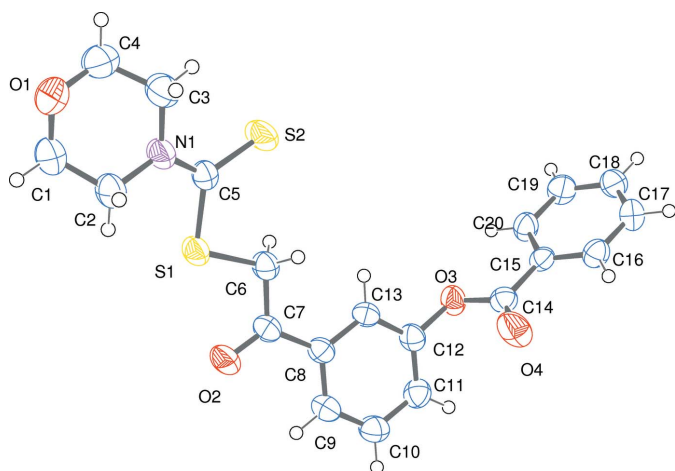


Figure 1
The molecular structure of the title compound, showing 50% displacement ellipsoids.

3. Supramolecular features

In the crystal, molecules are linked by weak C—H···O hydrogen bonds, forming zigzag chains along the *b* axis. C—H··· π interactions link centrosymmetrically related molecules, reinforcing the three-dimensional structure (Fig. 2)

4. Database survey

A search of the Cambridge Structural Database (Version 5.35, updates February 2014; Groom & Allen, 2014) for 2-(4-methoxyphenyl)-2-oxoethyl dithiocarbamate gave one hit, namely GEGGUV01 (Jian *et al.*, 2006). A search for 2-oxoethyl dithioformate gave two related structures, *viz.* 2-oxo-2-(2-oxo-2*H*-chromen-3-yl)ethyl pyrrolidine-1-carbodithioate (Kumar *et al.*, 2013) and (6-methoxy-2-oxo-2*H*-chromen-4-yl)methyl morpholine-4-carbodithioate (Devarajegowda *et al.*, 2013). Interestingly, dimer formation *via* C—H···O hydrogen bonds is a feature of the packing in these structures.

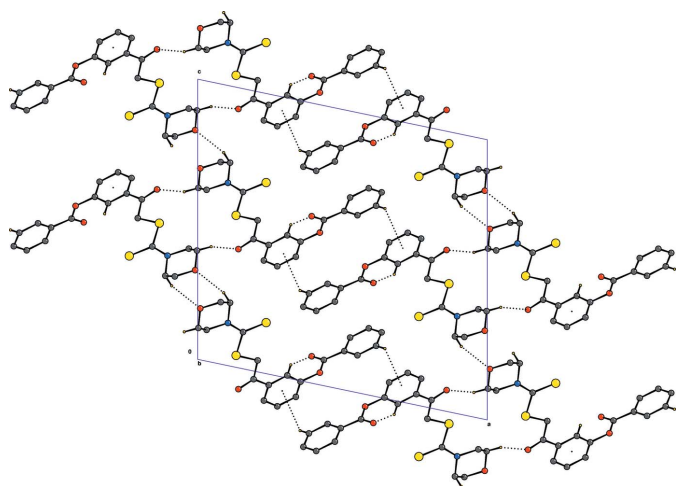


Figure 2
Packing diagram of the title compound, with C—H···O and C—H··· π interactions indicated by dashed lines.

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

C_g is the centroid of the C15–C20 ring.

D—H···A	D—H	H···A	D···A	D—H···A
C2—H2B···S1	0.97	2.41	2.938 (2)	114
C3—H3A···S2	0.97	2.56	3.052 (5)	111
C13—H13···O4 ⁱ	0.93	2.43	3.224 (3)	143
C11—H11···C _g ⁱⁱ	0.93	2.88	3.629 (2)	138

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

5. Synthesis and Crystallization

To a solution of NaOH (1 mmol) in 3 ml water was added to a mixture of morpholine (1 mmol) in ethanol (25 ml). After stirring at room temperature for about 20 min, carbon disulfide (1.2 mmol) was added dropwise and the resulting mixture was further stirred at room temperature for 90 min. Then 3-(2-bromacetyl) phenyl benzoate (1 mmol) was added and stirring was continued. After completion of the reaction (monitored by TLC), the solvent was removed under vacuum and the residue was extracted with dichloromethane (2 × 25 ml) and dried over anhydrous MgSO₄. The solvent was evaporated and the compound recrystallized from an ethanol–chloroform mixture (3:1) to give the title compound as colourless crystals in 81% yield.

Off-white solid, IR (KBr) $\nu_{\max}/\text{cm}^{-1}$: 2857, 3073 (C—H aliphatic and aromatic), 1732 (C=O), 1421, 1680 (C=C),

Table 2
Experimental details.

Crystal data	
Chemical formula	C ₂₀ H ₁₉ NO ₄ S ₂
<i>M</i> _r	401.48
Crystal system, space group	Monoclinic, <i>P</i> ₂ /c
Temperature (K)	296
<i>a</i> , <i>b</i> , <i>c</i> (Å)	19.5521 (7), 5.3649 (2), 18.5142 (6)
β (°)	101.816 (2)
<i>V</i> (Å ³)	1900.90 (12)
<i>Z</i>	4
Radiation type	Mo <i>K</i> α
μ (mm ⁻¹)	0.31
Crystal size (mm)	0.35 × 0.31 × 0.25
Data collection	
Diffractometer	Bruker SMART CCD area detector
Absorption correction	Multi-scan (SADABS; Sheldrick, 1996)
<i>T</i> _{min} , <i>T</i> _{max}	0.887, 0.934
No. of measured, independent and observed [<i>I</i> > 2 σ (<i>I</i>)] reflections	12830, 3539, 2613
<i>R</i> _{int}	0.024
(<i>sin</i> θ / λ) _{max} (Å ⁻¹)	0.606
Refinement	
$R[F^2 > 2\sigma(F^2)]$, <i>wR</i> (<i>F</i> ²), <i>S</i>	0.042, 0.122, 1.06
No. of reflections	3539
No. of parameters	244
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å ⁻³)	0.31, -0.22

Computer programs: SMART and SAINT (Bruker, 1998), SIR92 (Altomare *et al.*, 1993), SHELXL97 (Sheldrick, 2008), ORTEP-3 for Windows (Farrugia, 2012), CAMERON (Watkin *et al.*, 1993), PARST (Nardelli, 1995) and PLATON (Spek, 2009).

1264 (C—O), 1228 (C=S), 1061 (C—N). ¹H NMR (300 MHz, CDCl₃): δ 3.77–3.80 (*t*, 4H), 4.23–4.43 (*t*, 4H), 4.91(*s*, 2H), 7.26–7.47 (*m*, 1H), 7.48–7.51 (*m*, 2H), 7.53–7.60 (*m*, 1H), 7.63–7.68 (*m*, 1H), 7.90–7.91 (*t*, 1H), 7.99–8.02 (*d*, 1H), 8.20–8.22 (*d*, 2H); ¹³C NMR (75 MHz, CDCl₃): δ 44.6 (C6), 49.5 (C2, C3), 65.6 (C1, C4), 121.83 (C13), 126.0 (C9), 127.1 (C11), 128.6 (C10), 129.8 (C17, C19), 130.2 (C15, C16, C20), 137.6 (C18), 151.2 (C8), 154.93 (C12), 182.82 (C14), 192.15 (C7), 195.75 (C5); MS *m/z*: 402.10 [*M* + H]⁺. Analysis calculated (%) for C₂₀H₁₉NO₄S₂: C 59.83, H 4.77, N 3.49, S 15.97%; found: C 59.72, H 4.85, N 3.61, S 15.94.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The C-bound H atoms were positioned geometrically and allowed to ride on their parent atoms, with C—H = 0.93–0.97 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

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supporting information

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Crystal structure of 3-((morpholin-4-yl)carbonothioyl)sulfanyl)acetyl)phenyl benzoate

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Computing details

Data collection: *SMART* (Bruker, 1998); cell refinement: *SMART* (Bruker, 1998); data reduction: *SAINT* (Bruker, 1998); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012) and *CAMERON* (Watkin *et al.*, 1993); software used to prepare material for publication: *PARST* (Nardelli, 1995) and *PLATON* (Spek, 2009).

3-((Morpholin-4-yl)carbonothioyl)sulfanyl)acetyl)phenyl benzoate

Crystal data

C₂₀H₁₉NO₄S₂

M_r = 401.48

Monoclinic, *P*2₁/*c*

Hall symbol: -P 2ybc

a = 19.5521 (7) Å

b = 5.3649 (2) Å

c = 18.5142 (6) Å

β = 101.816 (2)°

V = 1900.90 (12) Å³

Z = 4

F(000) = 840

D_x = 1.403 Mg m⁻³

Mo *K*α radiation, λ = 0.71073 Å

θ = 1.5°

μ = 0.31 mm⁻¹

T = 296 K

Block, colourless

0.35 × 0.31 × 0.25 mm

Data collection

Bruker SMART CCD area-detector diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

φ and ω scans

Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)

T_{min} = 0.887, *T_{max}* = 0.934

12830 measured reflections

3539 independent reflections

2613 reflections with *I* > 2σ(*I*)

R_{int} = 0.024

θ_{max} = 25.5°, θ_{min} = 1.1°

h = -23→21

k = -6→6

l = -22→22

Refinement

Refinement on *F*²

Least-squares matrix: full

R[*F*² > 2σ(*F*²)] = 0.042

wR(*F*²) = 0.122

S = 1.06

3539 reflections

244 parameters

0 restraints

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0581P)^2 + 0.4768P]$$

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

$$\Delta\rho_{\max} = 0.31 \text{ e } \text{\AA}^{-3}$$

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

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.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
S1	0.13247 (3)	1.07076 (13)	0.54256 (3)	0.0473 (2)
S2	0.23625 (3)	1.18442 (16)	0.68201 (4)	0.0652 (3)
O1	0.00887 (10)	1.6886 (4)	0.68361 (10)	0.0733 (6)
O2	0.14049 (8)	0.7580 (4)	0.42396 (9)	0.0697 (6)
O3	0.42171 (7)	0.3229 (3)	0.54362 (8)	0.0483 (4)
O4	0.39360 (9)	-0.0264 (4)	0.59595 (10)	0.0741 (6)
N1	0.10421 (9)	1.3302 (4)	0.65235 (10)	0.0531 (6)
C1	0.00244 (13)	1.5923 (6)	0.61218 (14)	0.0639 (8)
H1A	0.0271	1.7004	0.5841	0.077*
H1B	-0.0465	1.5919	0.588	0.077*
C2	0.03069 (12)	1.3339 (5)	0.61164 (14)	0.0614 (8)
H2A	0.003	1.2205	0.6347	0.074*
H2B	0.0282	1.2798	0.5612	0.074*
C3	0.11178 (14)	1.4422 (6)	0.72615 (13)	0.0636 (8)
H3A	0.161	1.4564	0.7487	0.076*
H3B	0.0899	1.3352	0.7571	0.076*
C4	0.07911 (14)	1.6908 (6)	0.72117 (15)	0.0684 (8)
H4A	0.0816	1.7552	0.7706	0.082*
H4B	0.1053	1.8027	0.6959	0.082*
C5	0.15653 (11)	1.2086 (5)	0.63120 (11)	0.0413 (5)
C6	0.20694 (11)	0.8751 (5)	0.54092 (12)	0.0456 (6)
H6A	0.2483	0.9771	0.5431	0.055*
H6B	0.215	0.7648	0.5833	0.055*
C7	0.19298 (11)	0.7242 (5)	0.47079 (12)	0.0452 (6)
C8	0.24493 (10)	0.5309 (4)	0.46121 (11)	0.0395 (5)
C9	0.22848 (12)	0.3671 (5)	0.40227 (11)	0.0479 (6)
H9	0.1857	0.3808	0.3696	0.058*
C10	0.27482 (12)	0.1849 (5)	0.39175 (12)	0.0526 (7)
H10	0.263	0.075	0.3523	0.063*
C11	0.33890 (12)	0.1638 (5)	0.43933 (12)	0.0483 (6)
H11	0.3705	0.0409	0.4323	0.058*
C12	0.35499 (10)	0.3272 (5)	0.49695 (11)	0.0419 (6)

C13	0.30942 (10)	0.5091 (4)	0.50962 (11)	0.0414 (5)
H13	0.3214	0.616	0.5498	0.05*
C14	0.43558 (11)	0.1310 (5)	0.59189 (11)	0.0420 (5)
C15	0.50633 (10)	0.1476 (4)	0.63896 (11)	0.0372 (5)
C16	0.52631 (11)	-0.0360 (5)	0.69145 (12)	0.0453 (6)
H16	0.4962	-0.1674	0.695	0.054*
C17	0.59067 (12)	-0.0250 (5)	0.73859 (12)	0.0504 (6)
H17	0.604	-0.149	0.7738	0.061*
C18	0.63503 (12)	0.1690 (5)	0.73352 (13)	0.0513 (6)
H18	0.6783	0.1772	0.7656	0.062*
C19	0.61594 (12)	0.3512 (5)	0.68132 (14)	0.0541 (7)
H19	0.6464	0.4817	0.678	0.065*
C20	0.55158 (11)	0.3418 (5)	0.63371 (12)	0.0469 (6)
H20	0.5388	0.4654	0.5983	0.056*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0349 (3)	0.0585 (5)	0.0456 (3)	0.0066 (3)	0.0015 (2)	-0.0034 (3)
S2	0.0367 (3)	0.0894 (6)	0.0619 (4)	0.0102 (3)	-0.0081 (3)	-0.0198 (4)
O1	0.0666 (12)	0.0761 (15)	0.0765 (12)	0.0228 (11)	0.0129 (10)	-0.0131 (11)
O2	0.0453 (10)	0.0814 (15)	0.0702 (11)	0.0143 (10)	-0.0169 (8)	-0.0206 (10)
O3	0.0345 (8)	0.0437 (11)	0.0624 (9)	-0.0025 (7)	-0.0006 (7)	0.0083 (8)
O4	0.0600 (11)	0.0719 (15)	0.0788 (12)	-0.0315 (11)	-0.0128 (9)	0.0217 (10)
N1	0.0410 (11)	0.0666 (16)	0.0477 (11)	0.0127 (10)	-0.0001 (8)	-0.0080 (10)
C1	0.0484 (15)	0.071 (2)	0.0681 (17)	0.0092 (14)	0.0027 (12)	0.0023 (15)
C2	0.0393 (13)	0.076 (2)	0.0649 (15)	0.0129 (13)	0.0018 (11)	-0.0099 (14)
C3	0.0595 (16)	0.080 (2)	0.0498 (14)	0.0117 (15)	0.0066 (11)	-0.0060 (14)
C4	0.0686 (19)	0.069 (2)	0.0673 (17)	0.0034 (16)	0.0121 (14)	-0.0146 (15)
C5	0.0359 (11)	0.0424 (15)	0.0444 (11)	0.0010 (10)	0.0051 (9)	0.0039 (10)
C6	0.0334 (11)	0.0534 (17)	0.0481 (12)	0.0039 (11)	0.0041 (9)	-0.0035 (11)
C7	0.0341 (12)	0.0490 (17)	0.0492 (12)	-0.0040 (11)	0.0004 (9)	-0.0029 (11)
C8	0.0315 (11)	0.0433 (15)	0.0427 (11)	-0.0051 (10)	0.0049 (9)	-0.0010 (10)
C9	0.0429 (13)	0.0561 (18)	0.0417 (12)	-0.0031 (12)	0.0014 (10)	-0.0037 (11)
C10	0.0560 (15)	0.0570 (19)	0.0434 (12)	0.0016 (13)	0.0064 (11)	-0.0101 (11)
C11	0.0477 (13)	0.0488 (17)	0.0499 (13)	0.0060 (11)	0.0134 (10)	-0.0011 (11)
C12	0.0310 (11)	0.0450 (16)	0.0485 (12)	-0.0035 (10)	0.0055 (9)	0.0031 (10)
C13	0.0357 (11)	0.0413 (15)	0.0447 (12)	-0.0064 (10)	0.0024 (9)	-0.0039 (10)
C14	0.0400 (12)	0.0404 (16)	0.0456 (12)	-0.0030 (11)	0.0089 (9)	-0.0027 (10)
C15	0.0344 (11)	0.0326 (14)	0.0449 (11)	0.0006 (10)	0.0092 (9)	-0.0050 (10)
C16	0.0441 (13)	0.0379 (15)	0.0546 (13)	-0.0026 (11)	0.0121 (10)	0.0023 (11)
C17	0.0482 (14)	0.0488 (18)	0.0527 (13)	0.0085 (12)	0.0066 (11)	0.0091 (11)
C18	0.0379 (13)	0.0547 (18)	0.0571 (14)	0.0041 (12)	0.0004 (10)	-0.0041 (12)
C19	0.0384 (13)	0.0465 (18)	0.0740 (16)	-0.0093 (11)	0.0039 (11)	0.0008 (13)
C20	0.0410 (13)	0.0383 (16)	0.0592 (14)	-0.0014 (11)	0.0054 (10)	0.0063 (11)

Geometric parameters (Å, °)

S1—C5	1.774 (2)	C6—H6B	0.97
S1—C6	1.800 (2)	C7—C8	1.487 (3)
S2—C5	1.653 (2)	C8—C9	1.387 (3)
O1—C1	1.401 (3)	C8—C13	1.394 (3)
O1—C4	1.407 (3)	C9—C10	1.374 (3)
O2—C7	1.214 (2)	C9—H9	0.93
O3—C14	1.354 (3)	C10—C11	1.381 (3)
O3—C12	1.410 (2)	C10—H10	0.93
O4—C14	1.191 (3)	C11—C12	1.367 (3)
N1—C5	1.338 (3)	C11—H11	0.93
N1—C3	1.472 (3)	C12—C13	1.374 (3)
N1—C2	1.480 (3)	C13—H13	0.93
C1—C2	1.493 (4)	C14—C15	1.479 (3)
C1—H1A	0.97	C15—C16	1.382 (3)
C1—H1B	0.97	C15—C20	1.383 (3)
C2—H2A	0.97	C16—C17	1.378 (3)
C2—H2B	0.97	C16—H16	0.93
C3—C4	1.474 (4)	C17—C18	1.370 (3)
C3—H3A	0.97	C17—H17	0.93
C3—H3B	0.97	C18—C19	1.371 (3)
C4—H4A	0.97	C18—H18	0.93
C4—H4B	0.97	C19—C20	1.382 (3)
C6—C7	1.507 (3)	C19—H19	0.93
C6—H6A	0.97	C20—H20	0.93
C5—S1—C6	101.33 (10)	C8—C7—C6	118.02 (18)
C1—O1—C4	111.06 (19)	C9—C8—C13	119.1 (2)
C14—O3—C12	116.89 (17)	C9—C8—C7	118.78 (19)
C5—N1—C3	122.22 (19)	C13—C8—C7	122.1 (2)
C5—N1—C2	125.35 (19)	C10—C9—C8	120.6 (2)
C3—N1—C2	111.70 (18)	C10—C9—H9	119.7
O1—C1—C2	112.8 (2)	C8—C9—H9	119.7
O1—C1—H1A	109	C9—C10—C11	120.4 (2)
C2—C1—H1A	109	C9—C10—H10	119.8
O1—C1—H1B	109	C11—C10—H10	119.8
C2—C1—H1B	109	C12—C11—C10	118.6 (2)
H1A—C1—H1B	107.8	C12—C11—H11	120.7
N1—C2—C1	109.3 (2)	C10—C11—H11	120.7
N1—C2—H2A	109.8	C11—C12—C13	122.4 (2)
C1—C2—H2A	109.8	C11—C12—O3	120.3 (2)
N1—C2—H2B	109.8	C13—C12—O3	117.27 (19)
C1—C2—H2B	109.8	C12—C13—C8	118.9 (2)
H2A—C2—H2B	108.3	C12—C13—H13	120.6
N1—C3—C4	110.6 (2)	C8—C13—H13	120.6
N1—C3—H3A	109.5	O4—C14—O3	122.2 (2)
C4—C3—H3A	109.5	O4—C14—C15	125.4 (2)

N1—C3—H3B	109.5	O3—C14—C15	112.34 (19)
C4—C3—H3B	109.5	C16—C15—C20	119.5 (2)
H3A—C3—H3B	108.1	C16—C15—C14	117.8 (2)
O1—C4—C3	113.0 (2)	C20—C15—C14	122.6 (2)
O1—C4—H4A	109	C17—C16—C15	120.3 (2)
C3—C4—H4A	109	C17—C16—H16	119.8
O1—C4—H4B	109	C15—C16—H16	119.8
C3—C4—H4B	109	C18—C17—C16	119.8 (2)
H4A—C4—H4B	107.8	C18—C17—H17	120.1
N1—C5—S2	124.08 (17)	C16—C17—H17	120.1
N1—C5—S1	113.60 (15)	C17—C18—C19	120.3 (2)
S2—C5—S1	122.32 (13)	C17—C18—H18	119.8
C7—C6—S1	108.88 (15)	C19—C18—H18	119.8
C7—C6—H6A	109.9	C18—C19—C20	120.3 (2)
S1—C6—H6A	109.9	C18—C19—H19	119.9
C7—C6—H6B	109.9	C20—C19—H19	119.9
S1—C6—H6B	109.9	C19—C20—C15	119.7 (2)
H6A—C6—H6B	108.3	C19—C20—H20	120.2
O2—C7—C8	121.2 (2)	C15—C20—H20	120.2
O2—C7—C6	120.8 (2)		

Hydrogen-bond geometry (Å, °)

Cg is the centroid of the C15–C20 ring.

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
C2—H2B \cdots S1	0.97	2.41	2.938 (2)	114
C3—H3A \cdots S2	0.97	2.56	3.052 (5)	111
C13—H13 \cdots O4 ⁱ	0.93	2.43	3.224 (3)	143
C11—H11 \cdots Cg ⁱⁱ	0.93	2.88	3.629 (2)	138

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