



Crystal structure and Hirshfeld surface analysis of (Z)-4-oxo-4-{phenyl[(thiophen-2-yl)methyl]-amino}but-2-enoic acid

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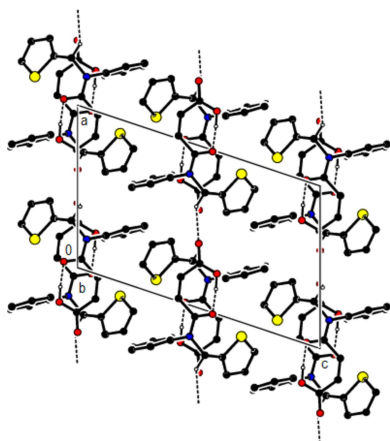
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In the title compound, C₁₅H₁₃NO₃S, the molecular conformation is stable with the intramolecular O—H···O hydrogen bond forming a *S*(7) ring motif. In the crystal, molecules are connected by C—H···O hydrogen bonds, forming *C*(8) chains running along the *a*-axis direction. Cohesion of the packing is provided by weak van der Waals interactions between the chains. A Hirshfeld surface analysis was undertaken to investigate and quantify the intermolecular interactions. The thiophene ring is disordered in a 0.9466 (17):0.0534 (17) ratio over two positions rotated by 180°.

1. Chemical context

The heterocyclic moiety of thiophene makes it a versatile building block for pharmaceuticals, polymers, and advanced materials (Abdelhamid *et al.*, 2011; Chawla *et al.*, 2023; Chan & Ng, 1998; Khalilov *et al.*, 2021; Safavora *et al.*, 2019). One of the interesting synthetic directions for thiophene is its introduction into the Diels–Alder reaction. Highly aromatic thiophene cannot undergo thermal or catalytic Diels–Alder reactions at normal pressure; special conditions are therefore required to fully unlock its synthetic potential in concerted cycloaddition reactions (Rulev & Zubkov, 2022; Polyanskii *et al.*, 2019). The first Diels–Alder adduct between thiophene and maleic anhydride, together with some of the simplest dienophiles, was synthesized under 17 kbar pressure and at almost room temperature (Kotsuki *et al.*, 1978; McCluskey *et al.*, 2002; Kumamoto *et al.*, 2004). Not only the thiophene moiety, but also its combination with other functional groups such as –COOH and C=O can be used as a synthetic strategy for the design of new catalysts, sensors or analytical reagents, and building blocks in crystal engineering (Kopylovich *et al.*, 2011, 2012a,b; MacLeod *et al.*, 2012; Mahmoudi *et al.*, 2017a,b; Mahmudov *et al.*, 2010, 2011; Martins *et al.*, 2017). The attached substituents can also participate in weak intermolecular interactions to direct the functional properties of new thiophene derivatives (Maharramov *et al.*, 2010; Mahmoudi *et al.*, 2019, 2021; Shikhaliyev *et al.*, 2019; Velásquez *et al.*, 2019). To further investigate the potential of thiophene derivatives as dienophiles in Diels–Alder reactions (see Krishna *et al.*, 2022), the title compound **1** was specifically designed and synthesized. The present work showcases a facile



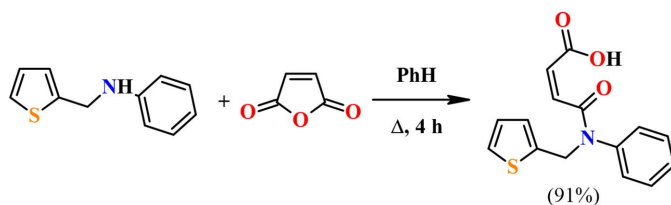
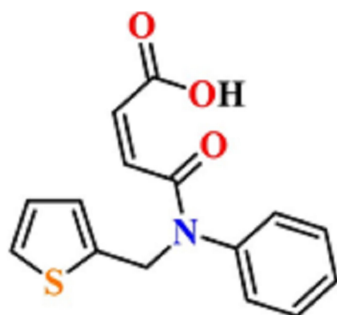


Figure 1
Preparation of the title compound.

methodology for the synthesis of compound **1** from a thiophene derivative and maleic anhydride – the title compound was isolated in a 91% yield after a standard treatment of the reaction mixture (Fig. 1).



2. Structural commentary

The molecular conformation of the title compound (Fig. 2) is stabilized by the intramolecular O—H...O hydrogen bond, which forms an *S*(7) ring motif (Bernstein *et al.*, 1995; Table 1).

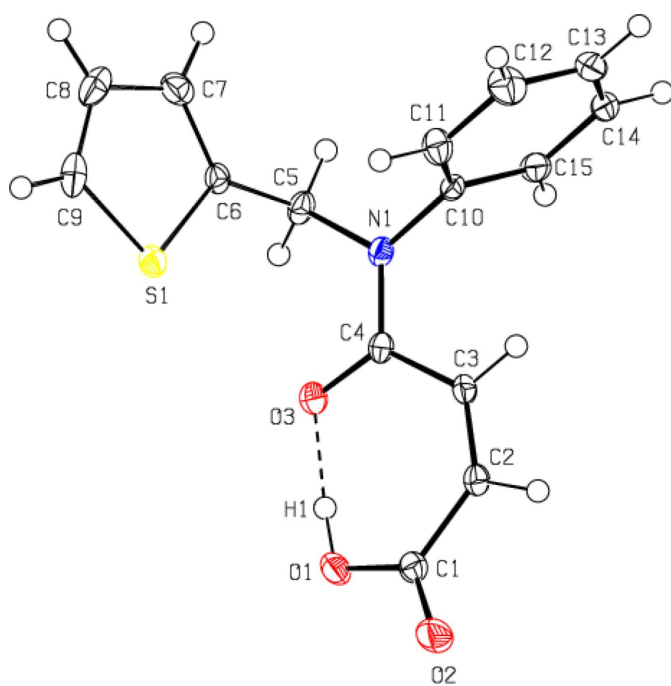


Figure 2
Molecular structure of the title compound showing the atom labelling and ellipsoids at the 50% probability level. Only the major disordered component is shown.

Table 1
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>
O1—H1...O3	0.93 (3)	1.59 (3)	2.5153 (15)	172 (2)
C5—H5B...O2 ⁱ	0.99	2.40	3.2201 (19)	140

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

The thiophene ring (S1/C6–C9) is disordered in a 0.9466 (17):0.0534 (17) ratio over two positions rotated by 180°. The phenyl ring (C10–C15) makes dihedral angles of 62.45 (8) and 63.1 (5)°, respectively, with the major and minor disorder components (S1/C6–C9 and S1A/C6A–C9A) of the thiophene ring. The sum of the angles around N1 of 359.9° is typical for secondary amides. The N1–C4–C3–C2, C4–C3–C2–C1, C3–C2–C1–O1 and C3–C2–C1–O2 torsion angles are 172.40 (13), –3.2 (2), 14.4 (2) and –165.63 (15)°, respectively. The bond lengths and angles in the title compound are comparable to those of the similar compounds reported in the *Database survey*.

3. Supramolecular features and Hirshfeld surface analysis

In the crystal, molecules are connected by C—H...O hydrogen bonds, forming *C*(8) chains running along the *a*-axis direction (Table 1; Figs. 3 and 4). Cohesion of the packing is provided by weak van der Waals interactions between the chains.

A Hirshfeld surface analysis was performed to further investigate the intermolecular interactions present in the title compound and the two-dimensional fingerprint plots were generated with *CrystalExplorer17.5* (Spackman *et al.*, 2021). Fig. 5 shows the three-dimensional Hirshfeld surface of the compound with d_{norm} (normalized contact distance) plotted over the range –0.2048 (red) to +1.3169 (blue) a.u.

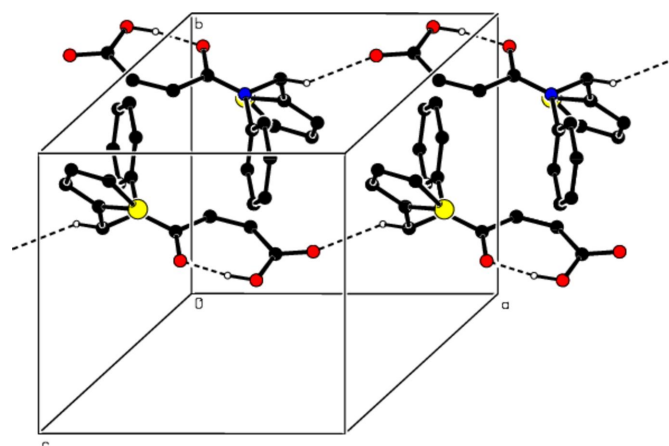


Figure 3
Crystal packing showing the chains along the *a*-axis direction formed by C—H...O and O—H...O hydrogen bonds (dashed lines). For clarity, the minor disordered component and H atoms not involved in hydrogen bonding were omitted.

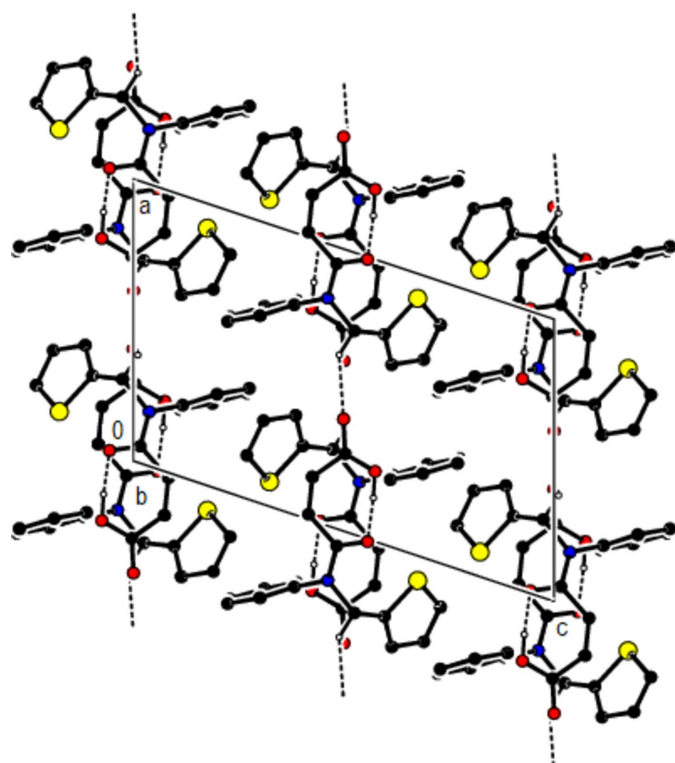


Figure 4
Crystal packing along the *b* axis showing C–H...O and O–H...O hydrogen bonds (dashed lines).

The fingerprint plots (Fig. 6) show that H...H [Fig. 6(b); 43.2%], C...H/H...C [Fig. 6(c); 27.7%] and O...H/H...O [Fig. 6(d); 23.7%] interactions contribute the most to the surface contacts. The percentage contributions to the Hirshfeld surfaces from other minor interatomic contacts are as follows: S...H/H...S 2.5%, C...O/O...C 1.0%, O...O 0.8%, C...C 0.5%, N...O/O...N 0.3% and S...O/O...S 0.2%.

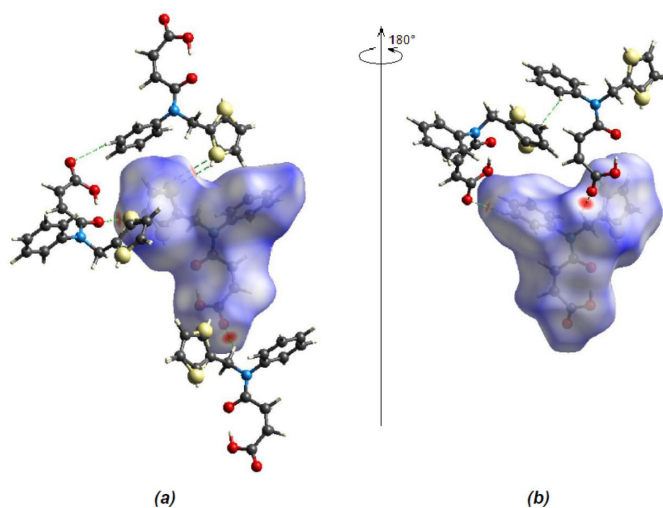


Figure 5
Front (a) and back (b) views of the three-dimensional Hirshfeld surface, with some C–H...O and O–H...O hydrogen bonds shown as dashed lines.

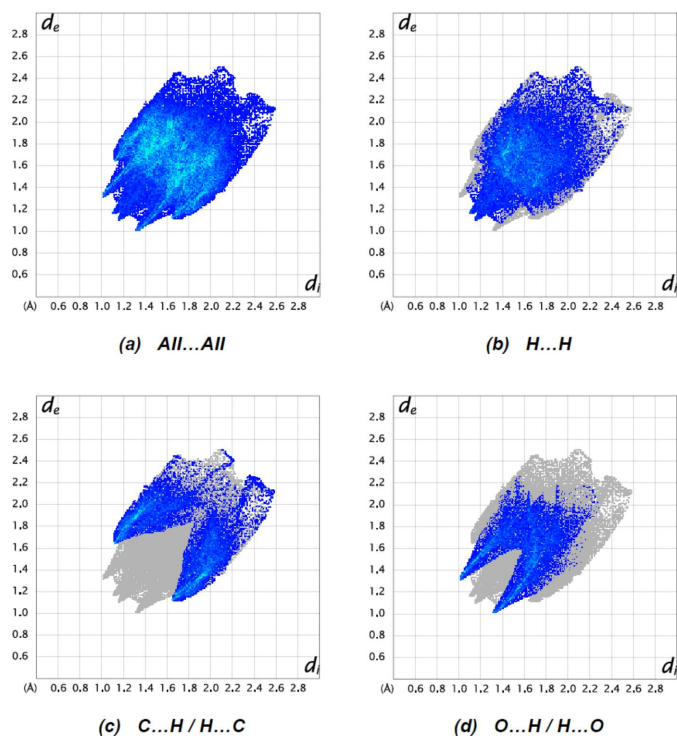


Figure 6
The two-dimensional fingerprint plots for the title molecule showing (a) all interactions, and delineated into (b) H...H, (c) C...H/H...C and (d) O...H/H...O interactions. The d_i and d_e values are the closest internal and external distances (in Å) from given points on the Hirshfeld surface.

4. Database survey

A search of the Cambridge Structural Database (CSD, version 5.43, update of June 2022; Groom *et al.*, 2016) for the *N*-[(thiophen-2-yl)methyl]aniline unit gave two similar structures, *viz.* 3,4-dimethyl-*N*-[1-(1-thiophen-2-yl)ethylidene]aniline (CSD refcode VIKXIY; Su *et al.*, 2013) and *N*-((*E*)-[5-[(*E*)-(pyridin-3-ylimino)methyl]thiophen-2-yl]methylidene)pyridin-3-amine (QIQLAF; Bolduc *et al.*, 2013). In VIKXIY, molecules are linked by non-classical C–H...N hydrogen bonds into supramolecular chains. The three-dimensional network of QIQLAF is governed by multiple weak interactions, including π -stacking between intercalated thiophene rings and azomethine bonds. The molecules are oriented in *anti* or *syn* orientations as a result of the hydrogen-bonding interactions in the crystal.

5. Synthesis and crystallization

A mixture of *N*-(thiophen-2-ylmethyl)aniline (1.89 g, 10 mmol) and maleic anhydride (0.98 g, 10 mmol) was refluxed for 4 h in benzene (20 mL) (TLC monitoring). The reaction mixture was then concentrated under reduced pressure and the obtained slightly yellow oil was solidified in hexane. The solid was recrystallized from a mixture of hexane/ethyl acetate (*v/v* ~5:4). The title compound was obtained as colourless prisms (2.61 g, 9.09 mmol). Yield 91%, m.p. 374.3–375.8 K. Single crystals were grown from a mixture of hexane/

ethyl acetate (~5:4). ^1H NMR (700 MHz, DMSO- d_6) (J , Hz): δ 12.75 (s , 1H), 7.41–7.37 (m , 1H), 7.36–7.31 (m , 2H), 7.31–7.26 (m , 1H), 7.18 (d , J = 7.3 Hz, 2H), 6.92–6.87 (m , 2H), 6.38 (d , J = 12.0, 1H), 5.78 (d , J = 12.0, 1H), 5.07 (s , 2H). ^{13}C NMR (175 MHz, CDCl_3): δ 165.87, 164.96, 139.69, 136.67, 136.36, 130.31, 129.63, 128.60, 128.50, 127.79, 126.78, 126.70, 48.81. HRMS (ESI–TOF): calculated for $\text{C}_{15}\text{H}_{13}\text{NO}_3\text{S}$ [$\text{M} + \text{H}$] $^+$ 288.0694; found 288.0691. Elemental analysis calculated (%) for $\text{C}_{15}\text{H}_{13}\text{NO}_3\text{S}$: C 62.70; H, 4.56; N, 4.87; O, 16.70; S, 11.16; found: C 62.82; H, 4.45; N, 4.94; O, 16.74; S, 11.04.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The thiophene ring (S1/C6–C9) is disordered in a ratio of 0.9466 (17): 0.0534 (17) over two positions with a rotation of 180° . C-bound H atoms were placed in their geometrically calculated positions and refined using a riding model, with C–H = 0.95–0.99 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ for aromatic and methylene H atoms. The H atom of the OH group was found in a difference-Fourier map and refined freely.

Acknowledgements

The authors' contributions are as follows. Conceptualization, MA and AB; synthesis, AGP and EVN; X-ray analysis, ZA; writing (review and editing of the manuscript), funding acquisition, ZA, EVN, MSG, KIH and NDS; supervision, MA and AB.

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Table 2

Experimental details.

Crystal data	
Chemical formula	$\text{C}_{15}\text{H}_{13}\text{NO}_3\text{S}$
M_r	287.32
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	100
a, b, c (Å)	9.8042 (8), 9.4258 (8), 15.4065 (13)
β ($^\circ$)	108.455 (3)
V (Å 3)	1350.5 (2)
Z	4
Radiation type	Mo $K\alpha$
μ (mm $^{-1}$)	0.25
Crystal size (mm)	0.40 × 0.34 × 0.20
Data collection	
Diffractometer	Bruker Kappa APEXII area-detector diffractometer
Absorption correction	Multi-scan (<i>SADABS</i> ; Krause <i>et al.</i> , 2015)
$T_{\text{min}}, T_{\text{max}}$	0.940, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	21582, 4012, 3177
R_{int}	0.043
$(\sin \theta/\lambda)_{\text{max}}$ (Å $^{-1}$)	0.708
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.038, 0.097, 1.03
No. of reflections	4012
No. of parameters	192
No. of restraints	12
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å $^{-3}$)	0.35, −0.34

Computer programs: *APEX4* and *SAINT* (Bruker, 2018), *SHELXT* (Sheldrick, 2015a), *SHELXL2018* (Sheldrick, 2015b), *ORTEP-3 for Windows* (Farrugia, 2012) and *PLATON* (Spek, 2020).

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Crystal structure and Hirshfeld surface analysis of (Z)-4-oxo-4-{phenyl[(thiophen-2-yl)methyl]amino}but-2-enoic acid

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Computing details

(Z)-4-Oxo-4-{phenyl[(thiophen-2-yl)methyl]amino}but-2-enoic acid

Crystal data

$C_{15}H_{13}NO_3S$

$M_r = 287.32$

Monoclinic, $P2_1/c$

$a = 9.8042(8) \text{ \AA}$

$b = 9.4258(8) \text{ \AA}$

$c = 15.4065(13) \text{ \AA}$

$\beta = 108.455(3)^\circ$

$V = 1350.5(2) \text{ \AA}^3$

$Z = 4$

$F(000) = 600$

$D_x = 1.413 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$

Cell parameters from 4604 reflections

$\theta = 2.8\text{--}29.0^\circ$

$\mu = 0.25 \text{ mm}^{-1}$

$T = 100 \text{ K}$

Bulk, colourless

$0.40 \times 0.34 \times 0.20 \text{ mm}$

Data collection

Bruker Kappa APEXII area-detector diffractometer

φ and ω scans

Absorption correction: multi-scan (SADABS; Krause *et al.*, 2015)

$T_{\min} = 0.940$, $T_{\max} = 1.000$

21582 measured reflections

4012 independent reflections

3177 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.043$

$\theta_{\max} = 30.2^\circ$, $\theta_{\min} = 3.0^\circ$

$h = -13 \rightarrow 13$

$k = -13 \rightarrow 13$

$l = -21 \rightarrow 21$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.038$

$wR(F^2) = 0.097$

$S = 1.03$

4012 reflections

192 parameters

12 restraints

Hydrogen site location: mixed

H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0437P)^2 + 0.4392P]$

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

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

$\Delta\rho_{\max} = 0.35 \text{ e \AA}^{-3}$

$\Delta\rho_{\min} = -0.34 \text{ e \AA}^{-3}$

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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
C1	1.27590 (14)	0.14305 (14)	0.00355 (9)	0.0182 (3)	
C2	1.15520 (14)	0.20128 (14)	-0.07416 (8)	0.0170 (3)	
H2	1.180897	0.219090	-0.127661	0.020*	
C3	1.01839 (14)	0.23331 (14)	-0.08348 (8)	0.0158 (2)	
H3	0.964652	0.274345	-0.140347	0.019*	
C4	0.93968 (14)	0.21300 (13)	-0.01641 (8)	0.0148 (2)	
C5	0.72253 (14)	0.24616 (15)	0.02527 (9)	0.0182 (3)	
H5A	0.748802	0.153057	0.055723	0.022*	
H5B	0.619115	0.242997	-0.010667	0.022*	
C6	0.74604 (14)	0.35914 (14)	0.09688 (8)	0.0158 (2)	0.9466 (17)
C7	0.6467 (2)	0.4469 (3)	0.11431 (18)	0.0227 (5)	0.9466 (17)
H7	0.548211	0.447362	0.078155	0.027*	0.9466 (17)
C8	0.70285 (18)	0.53646 (15)	0.19035 (10)	0.0260 (3)	0.9466 (17)
H8	0.647063	0.602554	0.211255	0.031*	0.9466 (17)
C9	0.84581 (17)	0.51709 (16)	0.23009 (9)	0.0247 (3)	0.9466 (17)
H9	0.902561	0.568587	0.281969	0.030*	0.9466 (17)
S1	0.91239 (4)	0.38895 (4)	0.17591 (2)	0.01947 (12)	0.9466 (17)
C6A	0.74604 (14)	0.35914 (14)	0.09688 (8)	0.0158 (2)	0.0534 (17)
C7A	0.866 (2)	0.409 (3)	0.1685 (14)	0.0227 (5)	0.0534 (17)
H7A	0.959121	0.372099	0.176104	0.027*	0.0534 (17)
C8A	0.84581 (17)	0.51709 (16)	0.23009 (9)	0.0247 (3)	0.0534 (17)
H8A	0.912101	0.560641	0.282056	0.030*	0.0534 (17)
C9A	0.70285 (18)	0.53646 (15)	0.19035 (10)	0.0260 (3)	0.0534 (17)
H9A	0.654641	0.604979	0.215253	0.031*	0.0534 (17)
S1A	0.6147 (12)	0.4493 (16)	0.1046 (9)	0.01947 (12)	0.0534 (17)
C10	0.74377 (13)	0.35644 (14)	-0.11738 (8)	0.0145 (2)	
C11	0.76237 (15)	0.50178 (15)	-0.11112 (9)	0.0218 (3)	
H11	0.815581	0.544184	-0.054609	0.026*	
C12	0.70262 (17)	0.58569 (16)	-0.18818 (11)	0.0281 (3)	
H12	0.714737	0.685746	-0.184435	0.034*	
C13	0.62523 (15)	0.52269 (17)	-0.27055 (10)	0.0264 (3)	
H13	0.585703	0.579641	-0.323445	0.032*	
C14	0.60560 (15)	0.37755 (17)	-0.27577 (9)	0.0248 (3)	
H14	0.551520	0.335301	-0.332142	0.030*	
C15	0.66448 (14)	0.29248 (16)	-0.19901 (9)	0.0205 (3)	
H15	0.650653	0.192624	-0.202446	0.025*	
N1	0.80705 (11)	0.26905 (12)	-0.03776 (7)	0.0152 (2)	
O1	1.24869 (11)	0.08523 (11)	0.07469 (6)	0.0217 (2)	
H1	1.153 (3)	0.100 (2)	0.0707 (15)	0.065 (7)*	

O2	1.39697 (11)	0.14995 (13)	-0.00031 (7)	0.0295 (3)
O3	0.99128 (10)	0.14570 (10)	0.05663 (6)	0.0200 (2)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0177 (6)	0.0198 (6)	0.0159 (6)	-0.0010 (5)	0.0038 (5)	-0.0025 (5)
C2	0.0193 (6)	0.0189 (6)	0.0136 (6)	-0.0008 (5)	0.0066 (5)	0.0015 (5)
C3	0.0178 (6)	0.0185 (6)	0.0112 (5)	0.0003 (5)	0.0047 (5)	0.0013 (4)
C4	0.0176 (6)	0.0137 (6)	0.0134 (5)	-0.0028 (5)	0.0054 (5)	-0.0022 (4)
C5	0.0175 (6)	0.0233 (7)	0.0168 (6)	-0.0040 (5)	0.0099 (5)	-0.0021 (5)
C6	0.0172 (6)	0.0188 (6)	0.0124 (5)	-0.0013 (5)	0.0062 (5)	0.0018 (4)
C7	0.0191 (11)	0.0285 (9)	0.0199 (10)	0.0011 (9)	0.0052 (9)	0.0066 (7)
C8	0.0398 (9)	0.0198 (7)	0.0266 (7)	0.0030 (6)	0.0223 (7)	0.0014 (5)
C9	0.0383 (8)	0.0224 (7)	0.0158 (6)	-0.0067 (6)	0.0120 (6)	-0.0037 (5)
S1	0.01743 (19)	0.0253 (2)	0.01436 (17)	-0.00051 (14)	0.00317 (13)	-0.00162 (13)
C6A	0.0172 (6)	0.0188 (6)	0.0124 (5)	-0.0013 (5)	0.0062 (5)	0.0018 (4)
C7A	0.0191 (11)	0.0285 (9)	0.0199 (10)	0.0011 (9)	0.0052 (9)	0.0066 (7)
C8A	0.0383 (8)	0.0224 (7)	0.0158 (6)	-0.0067 (6)	0.0120 (6)	-0.0037 (5)
C9A	0.0398 (9)	0.0198 (7)	0.0266 (7)	0.0030 (6)	0.0223 (7)	0.0014 (5)
S1A	0.01743 (19)	0.0253 (2)	0.01436 (17)	-0.00051 (14)	0.00317 (13)	-0.00162 (13)
C10	0.0124 (5)	0.0188 (6)	0.0131 (5)	0.0004 (4)	0.0051 (4)	-0.0020 (4)
C11	0.0256 (7)	0.0202 (7)	0.0179 (6)	-0.0035 (5)	0.0046 (5)	-0.0031 (5)
C12	0.0340 (8)	0.0208 (7)	0.0287 (8)	0.0009 (6)	0.0090 (6)	0.0044 (6)
C13	0.0223 (7)	0.0383 (9)	0.0194 (7)	0.0112 (6)	0.0077 (5)	0.0074 (6)
C14	0.0176 (6)	0.0385 (9)	0.0154 (6)	0.0071 (6)	0.0011 (5)	-0.0072 (6)
C15	0.0168 (6)	0.0228 (7)	0.0192 (6)	0.0020 (5)	0.0020 (5)	-0.0077 (5)
N1	0.0147 (5)	0.0185 (5)	0.0133 (5)	-0.0023 (4)	0.0059 (4)	-0.0017 (4)
O1	0.0193 (5)	0.0284 (5)	0.0159 (4)	0.0020 (4)	0.0033 (4)	0.0047 (4)
O2	0.0152 (5)	0.0472 (7)	0.0249 (5)	0.0013 (5)	0.0047 (4)	0.0033 (5)
O3	0.0229 (5)	0.0231 (5)	0.0155 (4)	0.0028 (4)	0.0080 (4)	0.0045 (3)

Geometric parameters (Å, °)

C1—O2	1.2089 (16)	C6A—C7A	1.414 (17)
C1—O1	1.3246 (16)	C6A—S1A	1.579 (12)
C1—C2	1.4960 (18)	C7A—C8A	1.447 (18)
C2—C3	1.3375 (18)	C7A—H7A	0.9500
C2—H2	0.9500	C8A—C9A	1.353 (2)
C3—C4	1.4848 (17)	C8A—H8A	0.9500
C3—H3	0.9500	C9A—S1A	1.563 (12)
C4—O3	1.2507 (15)	C9A—H9A	0.9500
C4—N1	1.3444 (16)	C10—C11	1.3813 (19)
C5—N1	1.4783 (16)	C10—C15	1.3895 (17)
C5—C6	1.4978 (18)	C10—N1	1.4444 (16)
C5—C6A	1.4978 (18)	C11—C12	1.392 (2)
C5—H5A	0.9900	C11—H11	0.9500
C5—H5B	0.9900	C12—C13	1.389 (2)

C6—C7	1.368 (3)	C12—H12	0.9500
C6—S1	1.7217 (13)	C13—C14	1.380 (2)
C7—C8	1.407 (3)	C13—H13	0.9500
C7—H7	0.9500	C14—C15	1.394 (2)
C8—C9	1.353 (2)	C14—H14	0.9500
C8—H8	0.9500	C15—H15	0.9500
C9—S1	1.7108 (15)	O1—H1	0.93 (3)
C9—H9	0.9500		
O2—C1—O1	121.40 (12)	C5—C6A—S1A	120.0 (4)
O2—C1—C2	118.76 (12)	C6A—C7A—C8A	119.6 (16)
O1—C1—C2	119.85 (12)	C6A—C7A—H7A	120.2
C3—C2—C1	132.93 (12)	C8A—C7A—H7A	120.2
C3—C2—H2	113.5	C9A—C8A—C7A	97.8 (8)
C1—C2—H2	113.5	C9A—C8A—H8A	131.1
C2—C3—C4	128.36 (12)	C7A—C8A—H8A	131.1
C2—C3—H3	115.8	C8A—C9A—S1A	121.9 (4)
C4—C3—H3	115.8	C8A—C9A—H9A	119.1
O3—C4—N1	120.25 (11)	S1A—C9A—H9A	119.1
O3—C4—C3	122.70 (12)	C9A—S1A—C6A	95.8 (6)
N1—C4—C3	117.04 (11)	C11—C10—C15	121.14 (12)
N1—C5—C6	113.11 (10)	C11—C10—N1	119.64 (11)
N1—C5—C6A	113.11 (10)	C15—C10—N1	119.22 (12)
N1—C5—H5A	109.0	C10—C11—C12	119.57 (13)
C6—C5—H5A	109.0	C10—C11—H11	120.2
N1—C5—H5B	109.0	C12—C11—H11	120.2
C6—C5—H5B	109.0	C13—C12—C11	119.80 (14)
H5A—C5—H5B	107.8	C13—C12—H12	120.1
C7—C6—C5	128.44 (15)	C11—C12—H12	120.1
C7—C6—S1	109.66 (13)	C14—C13—C12	120.18 (13)
C5—C6—S1	121.83 (10)	C14—C13—H13	119.9
C6—C7—C8	114.29 (17)	C12—C13—H13	119.9
C6—C7—H7	122.9	C13—C14—C15	120.54 (13)
C8—C7—H7	122.9	C13—C14—H14	119.7
C9—C8—C7	111.84 (15)	C15—C14—H14	119.7
C9—C8—H8	124.1	C10—C15—C14	118.76 (13)
C7—C8—H8	124.1	C10—C15—H15	120.6
C8—C9—S1	112.04 (11)	C14—C15—H15	120.6
C8—C9—H9	124.0	C4—N1—C10	123.64 (10)
S1—C9—H9	124.0	C4—N1—C5	118.81 (11)
C9—S1—C6	92.17 (7)	C10—N1—C5	117.49 (10)
C7A—C6A—C5	135.0 (9)	C1—O1—H1	110.4 (14)
C7A—C6A—S1A	104.9 (9)		
O2—C1—C2—C3	-165.63 (15)	C5—C6A—S1A—C9A	176.9 (3)
O1—C1—C2—C3	14.4 (2)	C15—C10—C11—C12	-1.0 (2)
C1—C2—C3—C4	-3.2 (2)	N1—C10—C11—C12	179.31 (12)
C2—C3—C4—O3	-8.5 (2)	C10—C11—C12—C13	-0.1 (2)

C2—C3—C4—N1	172.40 (13)	C11—C12—C13—C14	1.0 (2)
N1—C5—C6—C7	121.71 (19)	C12—C13—C14—C15	-0.8 (2)
N1—C5—C6—S1	-61.84 (14)	C11—C10—C15—C14	1.2 (2)
C5—C6—C7—C8	176.46 (15)	N1—C10—C15—C14	-179.09 (11)
S1—C6—C7—C8	-0.3 (2)	C13—C14—C15—C10	-0.3 (2)
C6—C7—C8—C9	0.6 (3)	O3—C4—N1—C10	175.49 (11)
C7—C8—C9—S1	-0.54 (19)	C3—C4—N1—C10	-5.36 (17)
C8—C9—S1—C6	0.30 (12)	O3—C4—N1—C5	-1.68 (17)
C7—C6—S1—C9	0.02 (15)	C3—C4—N1—C5	177.47 (11)
C5—C6—S1—C9	-177.02 (11)	C11—C10—N1—C4	-90.21 (15)
N1—C5—C6A—C7A	-61.1 (16)	C15—C10—N1—C4	90.09 (15)
N1—C5—C6A—S1A	121.4 (7)	C11—C10—N1—C5	87.00 (15)
C5—C6A—C7A—C8A	-175.6 (8)	C15—C10—N1—C5	-92.71 (14)
S1A—C6A—C7A—C8A	2 (2)	C6—C5—N1—C4	89.91 (14)
C6A—C7A—C8A—C9A	-2 (2)	C6A—C5—N1—C4	89.91 (14)
C7A—C8A—C9A—S1A	0.9 (13)	C6—C5—N1—C10	-87.43 (13)
C8A—C9A—S1A—C6A	0.2 (10)	C6A—C5—N1—C10	-87.43 (13)
C7A—C6A—S1A—C9A	-1.3 (15)		

Hydrogen-bond geometry (\AA , $^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1—H1 \cdots O3	0.93 (3)	1.59 (3)	2.5153 (15)	172 (2)
C5—H5B \cdots O2 ⁱ	0.99	2.40	3.2201 (19)	140
C9—H9 \cdots O3 ⁱⁱ	0.95	2.48	3.3904 (16)	160
C14—H14 \cdots O2 ⁱⁱⁱ	0.95	2.56	3.4261 (17)	152
C15—H15 \cdots Cg2 ^{iv}	0.95	3.00	3.504 (6)	115

Symmetry codes: (i) $x-1, y, z$; (ii) $-x+2, y+1/2, -z+1/2$; (iii) $x-1, -y+1/2, z-1/2$; (iv) $x, -y-1/2, z-3/2$.