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Crystal structure of 3-benzoyl-2-[(5-bromo-2-hydroxy-3-methoxybenzylidene)amino]-4,5,6,7-tetrahydrobenzo[*b*]thiophene

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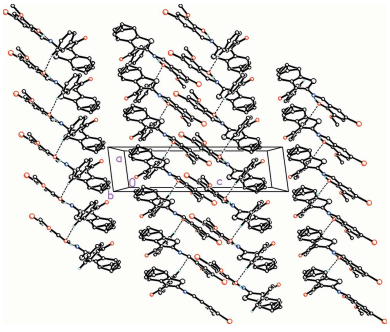
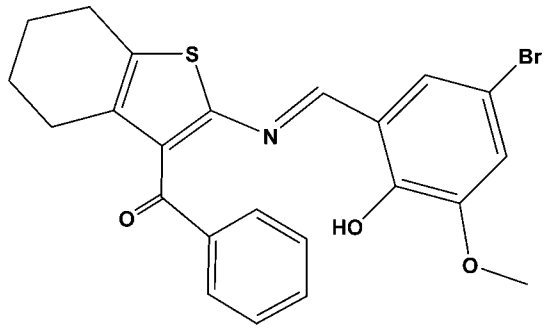
In the cyclohexene ring of the title compound, $C_{23}H_{20}BrNO_3S$, the $-(CH_2)_4-$ atoms are positionally disordered [occupancy ratio = 0.753 (6):0.247 (6)]. The ring has a half-chair conformation for both the major and minor components. The dihedral angles between the mean plane of the thiophene ring and those of the benzene and phenyl rings are 35.2 (4) and 57.7 (3)°, respectively. The planes of the two aryl rings are twisted with respect to each other by 86.4 (6)°. In the molecule, there is an O—H···N hydrogen bond forming an *S*(6) ring motif. In the crystal, molecules are linked *via* C—H···O hydrogen bonds, forming chains parallel to [100].

1. Chemical context

2-Aminothiophene derivatives have been used in a number of applications in pesticides, dyes and pharmaceuticals. Reviews on the synthesis and properties of these compounds have been reported (Sabnis *et al.* 1999; Puterová *et al.* 2010). Schiff base compounds are an important class of compounds both synthetically and biologically. These compounds show biological activities including antibacterial, antifungal, anticancer and herbicidal activities (Desai *et al.*, 2001; Karia & Parsania, 1999; Samadhiya & Halve, 2001; Singh & Dash, 1988). Furthermore, Schiff bases are utilized as starting materials in the synthesis of compounds of industrial (Aydogan *et al.*, 2001) and biological interest, such as β-lactams (Taggi *et al.*, 2002). The crystal and molecular structures of two 2-aminothiophenes have been reported by our group (Kubicki *et al.*, 2012). In a continuation of our work on Schiff base derivatives of 2-aminothiophenes, we report herein on the synthesis and crystal structure of the title Schiff base compound.





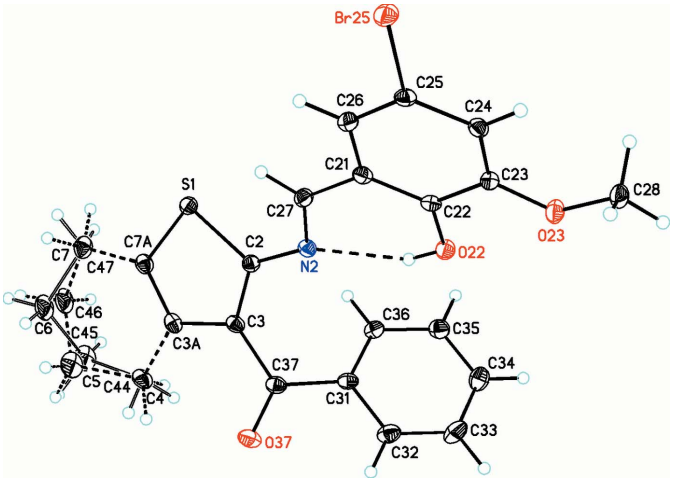


Figure 1
A view of the molecular structure of the title compound, showing the atom labelling. Displacement ellipsoids are drawn at the 30% probability level. The intramolecular hydrogen bond is shown as a dashed line (see Table 1 for details).

2. Structural commentary

In the title compound, Fig. 1, the cyclohexene ring is disordered with atoms C4/C44, C5/C45, C6/C46 and C7/C47 disordered about two positions with a refined occupancy ratio of 0.753 (6):0.247 (6). Both rings (C3*A*/C4–C7/C7*A*) and (C3*A*/C44–C47/C7*A*) adopt a half-chair conformation. The mean plane of the major component (C3*A*/C4–C7/C7*A*) is slightly twisted from the mean plane of the thiophene ring (S1/C2/C3/C3*A*/C7*A*) by 5.18 (14)°. The dihedral angles between the mean plane of the thiophene ring and the benzene (C21–C26) and phenyl (C31–C36) rings are 35.2 (4) and 57.7 (3)°, respectively. The two aryl rings are normal to each other, making a dihedral angle of 86.4 (6)°. In the molecule there is an O—H···N hydrogen bond forming an *S*(6) ring motif (Table 1 and Fig. 1).

3. Supramolecular features

In the crystal, molecules are linked *via* C—H···O hydrogen bonds, observed between the benzene and phenyl rings of adjacent molecules, forming chains parallel to the [100] direction (Fig. 2 and Table 1).

4. Database survey

A search of the Cambridge Structural Database (Version 5.36; Groom & Allen, 2014) for the substructure 4,5,6,7-tetrahydrobenzo[*b*]thiophene gave over 110 hits. Limiting the search to phenyl(4,5,6,7-tetrahydrobenzo[*b*]thiophen-3-yl)-methanone derivatives gave eight hits, which include five structures closely related to the title compound. These include [2-[(2-hydroxybenzylidene)amino][4,5,6,7-tetrahydro-1-benzothiophene-3-yl](phenyl)methanone (I) [QOCGAS; Kaur *et al.*, 2014*a*], [2-[(4-nitrobenzylidene)amino]-4,5,6,7-tetrahydro-1-benzothiophene-3-yl](phenyl)methanone (II) [SODGUP; Kaur *et al.*, 2014*b*], [2-(benzylideneamino)-4,5,6,7-tetrahydrobenzo[*b*]thiophen-3yl](phenyl)methanone (III) [YIYDAN; Kaur *et al.*, 2014*c*], [2-[(1*H*-indol-3-ylmethylidene)amino]-4,5,6,7-tetrahydrobenzo[*b*]thiophen-3-yl]-(phenyl)methanone (IV) [YIWJUL; Kaur *et al.*, 2014*d*] and [2-[2-bromo-5-methoxybenzylidene)amino]-4,5,6,7-tetrahydrobenzo[*b*]thiophene-3-yl](phenyl)methanone (V) [CIZYIV; Kaur *et al.*, 2014*e*]. Two of the compounds, (II) and (IV), crystallize in the monoclinic space group $P2_1$, while the others, including the title compound, crystallize in centrosymmetric monoclinic space groups.

A comparison of the structural properties of the title compound to these five closely related molecules reveals the following:

(*a*) The cyclohexene ring is disordered in compounds (II), (III), and (V), and has a slightly distorted half-chair conformation in (I), (III), (IV), and (V), and a distorted chair conformation in (II);

(*b*) The dihedral angle between the mean planes of the thiophene and phenyl rings is 70.4 (5)° in (I), *ca.* 63.6° in (II), 65.7 (3)° in (III), 63.0 (4) and 58.8 (9)° for the two independent molecules in (IV) and 66.1 (2)° in (V). The same dihedral angle in the title compound is 57.7 (3)°;

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O22—H22···N2	0.84	2.00	2.731 (3)	145
C35—H35···O22^{i}	0.95	2.54	3.212 (3)	128

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

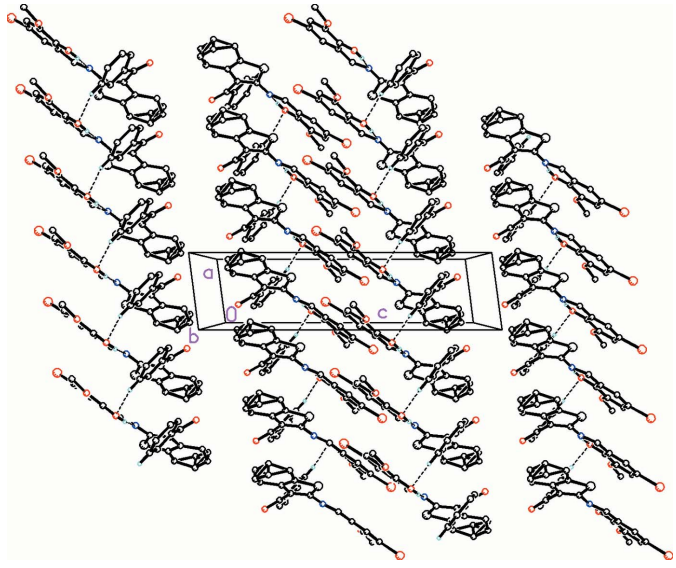


Figure 2
A view along the *b* axis of the crystal packing of the title compound. Dashed lines indicate weak C—H···O hydrogen bonds (see Table 1 for details; H atoms not involved in hydrogen bonding have been omitted for clarity).

(*c*) The dihedral angle between the mean planes of the thiophene and benzene rings is 12.1 (9)° in (I), 30.9 (8)° in (II), 8.3 (4)° in (III), 8.3 (5) and 6.7 (5)° for the two independent molecules in (IV) and 9.2 (2)° in (V). In the title compound this dihedral angle is 35.2 (4)°, similar to the situation in compound (III);

(*d*) In (I), (II), (III) and (V) the benzilidene and phenyl rings are inclined to one another by 81.0 (6), *ca*. 84.6, 73.8 (4) and 74.8 (8)°, respectively, compared to 86.4 (6)° in the title compound;

(*e*) There is an O—H···N intramolecular hydrogen bond in (I), as in the title compound;

(*f*) In the crystals of (I) and (III), C—H···O hydrogen bonds link molecules into chains along [100], as in the crystal of the title compound. In the crystal of (II), an array of C—H···O hydrogen bonds along [001] and [101] forms sheets parallel to (011). In the crystal of (IV), N—H···O hydrogen bonds link the molecules, forming chains along [101]. There are also π–π stacking interactions present, involving the thiophene and pyrrole rings of the two independent molecules, with an inter-centroid distance of 3.468 (2) Å. In the crystal of (V), molecules are linked by pairs of C—H···O hydrogen bonds, forming inversion dimers.

5. Synthesis and crystallization

To a solution of (2-amino-4,5,6,7-tetrahydro-benzo[*b*]thiophen-3-yl)-phenylmethanone (200 mg, 0.79 mmol) in 10 ml of methanol an equimolar amount of 5-bromo-2-hydroxy-3-methoxybenzaldehyde (183 mg, 0.79 mmol) was added with constant stirring. The mixture was refluxed for 6 h. A yellowish brown precipitate was obtained. Completion of the reaction was confirmed by thin layer chromatography. The precipitate obtained was filtered and dried at room temperature overnight. The solid was then recrystallized using a 1:1 solution of acetonitrile and dichloromethane, giving colourless block-like crystals.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. It was apparent from an early stage in the refinement that the saturated portion of the tetrahydrobenzothiophene unit exhibited conformational disorder over two sets of atomic sites having unequal occupancies. For the minor conformer, involving atoms C44–C47 (*cf*. Fig. 1), the bonded distances and the one-angle non-bonded distances were restrained to be the same as the corresponding distances in the major conformer, involving atoms C4–C7, subject to uncertainties of 0.005 and 0.01 Å, respectively. The atomic coordinates of atoms C4 and C44 were constrained to be identical, as were those of atoms C7 and C47. In addition, the anisotropic displacement parameters for pairs of partial-occupancy atoms occupying essentially the same physical space were constrained to be identical. The ratio of the occupancies of the disordered components refined to 0.753 (6):0.247 (6).

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{23}H_{20}BrNO_3S$
M_r	470.36
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	173
a, b, c (Å)	4.81267 (18), 22.1919 (8), 18.7012 (7)
β (°)	97.392 (3)
V (Å^3)	1980.73 (13)
Z	4
Radiation type	Cu $K\alpha$
μ (mm^{-1})	4.03
Crystal size (mm)	0.32 × 0.22 × 0.16
Data collection	
Diffractometer	Agilent Eos Gemini
Absorption correction	Multi-scan (*SADABS*; Sheldrick, 2008)
T_{min}, T_{max}	0.281, 0.525
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	7659, 3787, 3569
R_{int}	0.024
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.614
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.040, 0.108, 1.10
No. of reflections	3787
No. of parameters	271
No. of restraints	5
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.97, −0.47

Computer programs: *CrysAlis PRO* and *CrysAlis RED* (Agilent, 2012), *SHELXS97* (Sheldrick, 2008), *PLATON* (Spek, 2009) and *SHELXL2014* (Sheldrick, 2015).

The H atoms in the disordered portion of the molecule were included in the refinement in calculated positions, but all of the H atoms in the ordered portion of the molecule were located in difference maps. All the H atoms were then treated as riding atoms in geometrically idealized positions: O—H = 0.84 Å, C—H = 0.95–0.99 Å with U_{iso}(H) = 1.5U_{eq}(O,C) for the hydroxyl and methyl H atoms, and = 1.2U_{eq}(C) for other H atoms. A single weak outlier reflection ($\overline{4}$,13,14) was omitted from the refinement.

Acknowledgements

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Crystal structure of 3-benzoyl-2-[(5-bromo-2-hydroxy-3-methoxybenzylidene)amino]-4,5,6,7-tetrahydrobenzo[*b*]thiophene

Manpreet Kaur, Jerry P. Jasinski, H. S. Yathirajan, Christopher Glidewell and K. Byrappa

Computing details

Data collection: *CrysAlis PRO* (Agilent, 2012); cell refinement: *CrysAlis PRO* (Agilent, 2012); data reduction: *CrysAlis RED* (Agilent, 2012); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *PLATON* (Spek, 2009); software used to prepare material for publication: *PLATON* (Spek, 2009) and *SHELXL2014* (Sheldrick, 2015).

3-Benzoyl-2-[(5-bromo-2-hydroxy-3-methoxybenzylidene)amino]-4,5,6,7-tetrahydrobenzo[*b*]thiophene

Crystal data

$C_{23}H_{20}BrNO_3S$
M_r = 470.36
Monoclinic, $P2_1/c$
a = 4.81267 (18) Å
b = 22.1919 (8) Å
c = 18.7012 (7) Å
β = 97.392 (3)°
V = 1980.73 (13) Å^3
Z = 4
$F(000)$ = 960
D_x = 1.577 Mg m^{-3}
Cu $K\alpha$ radiation, λ = 1.54184 Å
Cell parameters from 3787 reflections
θ = 4.0–71.1°
μ = 4.03 mm^{-1}
T = 173 K
Block, colourless
0.32 × 0.22 × 0.16 mm

Data collection

Agilent Eos Gemini diffractometer
Radiation source: Enhance (Cu) X-ray Source
Detector resolution: 16.0416 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2008)
T_{min} = 0.281, T_{max} = 0.525
7659 measured reflections
3787 independent reflections
3569 reflections with $I > 2\sigma(I)$
R_{int} = 0.024
θ_{max} = 71.1°, θ_{min} = 4.0°
h = −5→4
k = −23→27
l = −19→22

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.040
$wR(F^2)$ = 0.108
S = 1.10
3787 reflections
271 parameters
5 restraints
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0688P)^2 + 1.0707P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.97 e Å^{-3}
$\Delta\rho_{min}$ = −0.47 e Å^{-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 (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
S1	0.69785 (12)	0.48921 (2)	0.30795 (3)	0.02408 (15)	
C2	0.5317 (5)	0.42375 (10)	0.27216 (12)	0.0209 (5)	
C3	0.5569 (5)	0.41833 (10)	0.19965 (12)	0.0217 (5)	
C3A	0.7019 (5)	0.46860 (11)	0.17283 (12)	0.0230 (5)	
C4	0.7525 (5)	0.47825 (12)	0.09563 (13)	0.0292 (5)	0.753 (6)
H4A	0.5712	0.4860	0.0656	0.035*	0.753 (6)
H4B	0.8335	0.4411	0.0775	0.035*	0.753 (6)
C5	0.9516 (10)	0.53138 (18)	0.0881 (2)	0.0417 (11)	0.753 (6)
H5A	1.1474	0.5171	0.0987	0.050*	0.753 (6)
H5B	0.9236	0.5457	0.0375	0.050*	0.753 (6)
C6	0.9090 (10)	0.58370 (16)	0.1374 (2)	0.0405 (10)	0.753 (6)
H6A	0.7144	0.5988	0.1267	0.049*	0.753 (6)
H6B	1.0376	0.6169	0.1287	0.049*	0.753 (6)
C7	0.9640 (6)	0.56445 (12)	0.21574 (15)	0.0316 (5)	0.753 (6)
H7A	1.1660	0.5560	0.2292	0.038*	0.753 (6)
H7B	0.9093	0.5971	0.2472	0.038*	0.753 (6)
C44	0.7525 (5)	0.47825 (12)	0.09563 (13)	0.0292 (5)	0.247 (6)
H44A	0.5808	0.4681	0.0628	0.035*	0.247 (6)
H44B	0.9051	0.4514	0.0842	0.035*	0.247 (6)
C45	0.833 (3)	0.5441 (3)	0.0844 (4)	0.0417 (11)	0.247 (6)
H45A	0.8962	0.5485	0.0364	0.050*	0.247 (6)
H45B	0.6657	0.5700	0.0856	0.050*	0.247 (6)
C46	1.063 (2)	0.5648 (5)	0.1419 (3)	0.0405 (10)	0.247 (6)
H46A	1.1222	0.6060	0.1305	0.049*	0.247 (6)
H46B	1.2268	0.5378	0.1423	0.049*	0.247 (6)
C47	0.9640 (6)	0.56445 (12)	0.21574 (15)	0.0316 (5)	0.247 (6)
H47A	1.1281	0.5659	0.2535	0.038*	0.247 (6)
H47B	0.8480	0.6006	0.2211	0.038*	0.247 (6)
C7A	0.7954 (5)	0.50878 (11)	0.22528 (13)	0.0248 (5)	
N2	0.3809 (4)	0.38630 (9)	0.31246 (10)	0.0214 (4)	
C27	0.2835 (5)	0.40820 (11)	0.36777 (12)	0.0228 (5)	
H27	0.3226	0.4492	0.3798	0.027*	
C21	0.1168 (5)	0.37392 (10)	0.41313 (12)	0.0213 (4)	
C22	0.0790 (4)	0.31190 (10)	0.40655 (11)	0.0199 (4)	
C23	−0.0965 (5)	0.28198 (10)	0.45045 (12)	0.0214 (4)	
C24	−0.2273 (5)	0.31462 (10)	0.49988 (12)	0.0216 (4)	
H24	−0.3471	0.2950	0.5291	0.026*	
C25	−0.1808 (5)	0.37664 (10)	0.50617 (12)	0.0221 (4)	
Br25	−0.34996 (6)	0.42100 (2)	0.57603 (2)	0.03072 (12)	

C26	−0.0130 (5)	0.40670 (11)	0.46400 (12)	0.0242 (5)
H26	0.0150	0.4489	0.4691	0.029*
O22	0.2048 (4)	0.27806 (7)	0.35966 (9)	0.0251 (3)
H22	0.2957	0.3006	0.3350	0.038*
O23	−0.1211 (4)	0.22165 (8)	0.44037 (10)	0.0286 (4)
C28	−0.3190 (5)	0.19060 (11)	0.47808 (14)	0.0298 (5)
H28A	−0.5067	0.2072	0.4638	0.045*
H28B	−0.2674	0.1958	0.5301	0.045*
H28C	−0.3183	0.1476	0.4661	0.045*
C37	0.4280 (5)	0.36935 (11)	0.15198 (12)	0.0241 (5)
O37	0.3043 (4)	0.38180 (9)	0.09281 (10)	0.0383 (5)
C31	0.4593 (5)	0.30534 (11)	0.17603 (12)	0.0225 (4)
C32	0.2770 (5)	0.26251 (12)	0.14146 (14)	0.0314 (5)
H32	0.1365	0.2746	0.1038	0.038*
C33	0.2995 (6)	0.20244 (13)	0.16173 (17)	0.0377 (6)
H33	0.1737	0.1735	0.1384	0.045*
C34	0.5061 (6)	0.18479 (12)	0.21618 (16)	0.0344 (6)
H34	0.5205	0.1437	0.2302	0.041*
C35	0.6910 (5)	0.22637 (12)	0.25018 (14)	0.0305 (5)
H35	0.8332	0.2138	0.2872	0.037*
C36	0.6684 (5)	0.28688 (11)	0.23010 (13)	0.0255 (5)
H36	0.7960	0.3156	0.2533	0.031*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0302 (3)	0.0230 (3)	0.0203 (3)	−0.0042 (2)	0.0079 (2)	−0.0015 (2)
C2	0.0232 (11)	0.0205 (10)	0.0191 (11)	0.0011 (8)	0.0037 (8)	−0.0007 (8)
C3	0.0228 (11)	0.0244 (11)	0.0183 (11)	0.0047 (8)	0.0042 (8)	0.0013 (8)
C3A	0.0218 (11)	0.0254 (11)	0.0232 (11)	0.0045 (9)	0.0084 (8)	0.0049 (9)
C4	0.0350 (13)	0.0341 (13)	0.0204 (11)	0.0045 (10)	0.0108 (9)	0.0041 (10)
C5	0.055 (3)	0.041 (2)	0.0355 (17)	−0.005 (2)	0.030 (2)	0.0059 (15)
C6	0.056 (3)	0.0313 (19)	0.0381 (19)	−0.0044 (16)	0.0191 (19)	0.0105 (15)
C7	0.0347 (13)	0.0265 (12)	0.0356 (14)	−0.0045 (10)	0.0120 (11)	0.0022 (11)
C44	0.0350 (13)	0.0341 (13)	0.0204 (11)	0.0045 (10)	0.0108 (9)	0.0041 (10)
C45	0.055 (3)	0.041 (2)	0.0355 (17)	−0.005 (2)	0.030 (2)	0.0059 (15)
C46	0.056 (3)	0.0313 (19)	0.0381 (19)	−0.0044 (16)	0.0191 (19)	0.0105 (15)
C47	0.0347 (13)	0.0265 (12)	0.0356 (14)	−0.0045 (10)	0.0120 (11)	0.0022 (11)
C7A	0.0264 (11)	0.0251 (11)	0.0239 (11)	0.0025 (9)	0.0077 (9)	0.0034 (9)
N2	0.0231 (9)	0.0230 (9)	0.0185 (8)	−0.0013 (7)	0.0039 (7)	0.0005 (7)
C27	0.0257 (11)	0.0213 (10)	0.0222 (11)	−0.0024 (9)	0.0055 (9)	−0.0023 (9)
C21	0.0220 (10)	0.0249 (11)	0.0170 (10)	−0.0009 (9)	0.0024 (8)	0.0002 (8)
C22	0.0194 (10)	0.0249 (11)	0.0149 (9)	0.0013 (8)	0.0002 (7)	−0.0013 (8)
C23	0.0239 (11)	0.0201 (10)	0.0195 (10)	−0.0016 (8)	0.0006 (8)	0.0005 (8)
C24	0.0221 (10)	0.0249 (11)	0.0180 (10)	−0.0033 (8)	0.0036 (8)	0.0015 (8)
C25	0.0250 (11)	0.0253 (11)	0.0168 (10)	0.0004 (9)	0.0052 (8)	−0.0035 (8)
Br25	0.04036 (19)	0.02851 (18)	0.02633 (17)	−0.00364 (10)	0.01589 (12)	−0.00703 (9)
C26	0.0286 (12)	0.0232 (10)	0.0212 (10)	−0.0024 (9)	0.0044 (9)	−0.0023 (9)

O22	0.0293 (9)	0.0237 (8)	0.0240 (8)	−0.0016 (6)	0.0099 (6)	−0.0028 (6)
O23	0.0361 (9)	0.0206 (8)	0.0314 (8)	−0.0038 (7)	0.0141 (7)	−0.0009 (7)
C28	0.0344 (13)	0.0248 (11)	0.0315 (12)	−0.0091 (10)	0.0094 (10)	0.0014 (10)
C37	0.0241 (11)	0.0288 (12)	0.0198 (10)	0.0029 (9)	0.0037 (8)	−0.0023 (9)
O37	0.0496 (11)	0.0379 (10)	0.0241 (9)	0.0043 (9)	−0.0088 (8)	0.0008 (8)
C31	0.0215 (10)	0.0279 (12)	0.0185 (10)	0.0025 (9)	0.0043 (8)	−0.0048 (9)
C32	0.0270 (12)	0.0334 (13)	0.0316 (12)	0.0023 (10)	−0.0044 (10)	−0.0071 (11)
C33	0.0310 (13)	0.0318 (13)	0.0484 (16)	−0.0062 (11)	−0.0025 (11)	−0.0100 (12)
C34	0.0349 (13)	0.0248 (12)	0.0441 (15)	0.0034 (10)	0.0076 (11)	−0.0022 (11)
C35	0.0314 (12)	0.0302 (13)	0.0289 (12)	0.0060 (10)	0.0003 (10)	−0.0012 (10)
C36	0.0247 (11)	0.0257 (11)	0.0256 (11)	0.0004 (9)	0.0009 (9)	−0.0043 (9)

Geometric parameters (Å, º)

S1—C7A	1.728 (2)	C21—C26	1.406 (3)
S1—C2	1.749 (2)	C22—O22	1.355 (3)
C2—C3	1.382 (3)	C22—C23	1.417 (3)
C2—N2	1.388 (3)	C23—O23	1.355 (3)
C3—C3A	1.440 (3)	C23—C24	1.387 (3)
C3—C37	1.490 (3)	C24—C25	1.397 (3)
C3A—C7A	1.359 (3)	C24—H24	0.9500
C3A—C4	1.510 (3)	C25—C26	1.372 (3)
C4—C5	1.537 (4)	C25—Br25	1.901 (2)
C4—H4A	0.9900	C26—H26	0.9500
C4—H4B	0.9900	O22—H22	0.8400
C5—C6	1.514 (5)	O23—C28	1.433 (3)
C5—H5A	0.9900	C28—H28A	0.9800
C5—H5B	0.9900	C28—H28B	0.9800
C6—C7	1.516 (4)	C28—H28C	0.9800
C6—H6A	0.9900	C37—O37	1.219 (3)
C6—H6B	0.9900	C37—C31	1.492 (3)
C7—C7A	1.501 (3)	C31—C36	1.394 (3)
C7—H7A	0.9900	C31—C32	1.395 (3)
C7—H7B	0.9900	C32—C33	1.386 (4)
C45—C46	1.512 (7)	C32—H32	0.9500
C45—H45A	0.9900	C33—C34	1.385 (4)
C45—H45B	0.9900	C33—H33	0.9500
C46—H46A	0.9900	C34—C35	1.379 (4)
C46—H46B	0.9900	C34—H34	0.9500
N2—C27	1.285 (3)	C35—C36	1.395 (4)
C27—C21	1.455 (3)	C35—H35	0.9500
C27—H27	0.9500	C36—H36	0.9500
C21—C22	1.392 (3)		

C7A—S1—C2	91.71 (12)	C22—C21—C26	120.5 (2)
C3—C2—N2	126.8 (2)	C22—C21—C27	122.8 (2)
C3—C2—S1	110.73 (17)	C26—C21—C27	116.7 (2)
N2—C2—S1	122.33 (17)	O22—C22—C21	122.8 (2)

C2—C3—C3A	112.5 (2)	O22—C22—C23	117.7 (2)
C2—C3—C37	124.6 (2)	C21—C22—C23	119.5 (2)
C3A—C3—C37	122.7 (2)	O23—C23—C24	124.7 (2)
C7A—C3A—C3	112.8 (2)	O23—C23—C22	115.5 (2)
C7A—C3A—C4	121.2 (2)	C24—C23—C22	119.8 (2)
C3—C3A—C4	126.0 (2)	C23—C24—C25	119.3 (2)
C3A—C4—C5	112.1 (2)	C23—C24—H24	120.4
C3A—C4—H4A	109.2	C25—C24—H24	120.4
C5—C4—H4A	109.2	C26—C25—C24	122.0 (2)
C3A—C4—H4B	109.2	C26—C25—Br25	118.62 (18)
C5—C4—H4B	109.2	C24—C25—Br25	119.34 (17)
H4A—C4—H4B	107.9	C25—C26—C21	118.9 (2)
C6—C5—C4	113.4 (3)	C25—C26—H26	120.6
C6—C5—H5A	108.9	C21—C26—H26	120.6
C4—C5—H5A	108.9	C22—O22—H22	109.5
C6—C5—H5B	108.9	C23—O23—C28	117.29 (19)
C4—C5—H5B	108.9	O23—C28—H28A	109.5
H5A—C5—H5B	107.7	O23—C28—H28B	109.5
C5—C6—C7	110.6 (3)	H28A—C28—H28B	109.5
C5—C6—H6A	109.5	O23—C28—H28C	109.5
C7—C6—H6A	109.5	H28A—C28—H28C	109.5
C5—C6—H6B	109.5	H28B—C28—H28C	109.5
C7—C6—H6B	109.5	O37—C37—C3	119.7 (2)
H6A—C6—H6B	108.1	O37—C37—C31	120.5 (2)
C7A—C7—C6	108.5 (2)	C3—C37—C31	119.8 (2)
C7A—C7—H7A	110.0	C36—C31—C32	119.2 (2)
C6—C7—H7A	110.0	C36—C31—C37	122.3 (2)
C7A—C7—H7B	110.0	C32—C31—C37	118.4 (2)
C6—C7—H7B	110.0	C33—C32—C31	120.4 (2)
H7A—C7—H7B	108.4	C33—C32—H32	119.8
C46—C45—H45A	109.3	C31—C32—H32	119.8
C46—C45—H45B	109.3	C34—C33—C32	119.8 (2)
H45A—C45—H45B	108.0	C34—C33—H33	120.1
C45—C46—H46A	109.4	C32—C33—H33	120.1
C45—C46—H46B	109.4	C35—C34—C33	120.6 (3)
H46A—C46—H46B	108.0	C35—C34—H34	119.7
C3A—C7A—C7	126.0 (2)	C33—C34—H34	119.7
C3A—C7A—S1	112.21 (18)	C34—C35—C36	119.8 (2)
C7—C7A—S1	121.76 (19)	C34—C35—H35	120.1
C27—N2—C2	118.8 (2)	C36—C35—H35	120.1
N2—C27—C21	123.9 (2)	C31—C36—C35	120.2 (2)
N2—C27—H27	118.1	C31—C36—H36	119.9
C21—C27—H27	118.1	C35—C36—H36	119.9

C7A—S1—C2—C3	0.59 (18)	C27—C21—C22—C23	−177.2 (2)
C7A—S1—C2—N2	−175.17 (19)	O22—C22—C23—O23	−0.3 (3)
N2—C2—C3—C3A	173.3 (2)	C21—C22—C23—O23	180.0 (2)
S1—C2—C3—C3A	−2.2 (2)	O22—C22—C23—C24	179.26 (19)

N2—C2—C3—C37	−1.4 (4)	C21—C22—C23—C24	−0.5 (3)
S1—C2—C3—C37	−176.97 (18)	O23—C23—C24—C25	178.7 (2)
C2—C3—C3A—C7A	3.3 (3)	C22—C23—C24—C25	−0.8 (3)
C37—C3—C3A—C7A	178.1 (2)	C23—C24—C25—C26	1.2 (3)
C2—C3—C3A—C4	−176.9 (2)	C23—C24—C25—Br25	−177.96 (16)
C37—C3—C3A—C4	−2.0 (4)	C24—C25—C26—C21	−0.3 (3)
C7A—C3A—C4—C5	8.5 (4)	Br25—C25—C26—C21	178.87 (17)
C3—C3A—C4—C5	−171.4 (3)	C22—C21—C26—C25	−1.0 (3)
C3A—C4—C5—C6	−37.5 (4)	C27—C21—C26—C25	177.6 (2)
C4—C5—C6—C7	61.4 (5)	C24—C23—O23—C28	6.8 (3)
C5—C6—C7—C7A	−51.5 (4)	C22—C23—O23—C28	−173.6 (2)
C3—C3A—C7A—C7	177.3 (2)	C2—C3—C37—O37	133.9 (3)
C4—C3A—C7A—C7	−2.6 (4)	C3A—C3—C37—O37	−40.3 (3)
C3—C3A—C7A—S1	−2.8 (3)	C2—C3—C37—C31	−48.1 (3)
C4—C3A—C7A—S1	177.36 (18)	C3A—C3—C37—C31	137.7 (2)
C6—C7—C7A—C3A	24.3 (4)	O37—C37—C31—C36	158.4 (2)
C6—C7—C7A—S1	−155.6 (2)	C3—C37—C31—C36	−19.6 (3)
C2—S1—C7A—C3A	1.30 (19)	O37—C37—C31—C32	−19.7 (4)
C2—S1—C7A—C7	−178.8 (2)	C3—C37—C31—C32	162.3 (2)
C3—C2—N2—C27	−152.3 (2)	C36—C31—C32—C33	1.4 (4)
S1—C2—N2—C27	22.7 (3)	C37—C31—C32—C33	179.6 (2)
C2—N2—C27—C21	178.5 (2)	C31—C32—C33—C34	−0.6 (4)
N2—C27—C21—C22	9.0 (4)	C32—C33—C34—C35	−0.4 (5)
N2—C27—C21—C26	−169.6 (2)	C33—C34—C35—C36	0.6 (4)
C26—C21—C22—O22	−178.3 (2)	C32—C31—C36—C35	−1.2 (4)
C27—C21—C22—O22	3.1 (3)	C37—C31—C36—C35	−179.3 (2)
C26—C21—C22—C23	1.4 (3)	C34—C35—C36—C31	0.2 (4)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O22—H22···N2	0.84	2.00	2.731 (3)	145
C35—H35···O22^{i}	0.95	2.54	3.212 (3)	128

Symmetry code: (i) *x*+1, *y*, *z*.