

# Crystal structures of 4-[(4-methylbenzyl)oxy]-benzohydrazide and its *N'*-[(thiophen-2-yl)methylidene]- derivative

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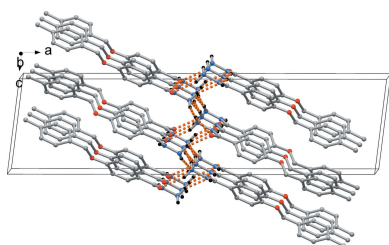
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The molecular and crystal structures of a benzoylhydrazine bearing an ether group, 4-[(4-methylbenzyl)oxy]benzohydrazide, C<sub>15</sub>H<sub>16</sub>N<sub>2</sub>O<sub>2</sub>, (I), and of the corresponding *N'*-[(thiophen-2-yl)methylidene]- derivative, 4-[(4-methylbenzyl)oxy]-*N'*-[(thiophen-2-yl)methylidene]benzohydrazide, C<sub>20</sub>H<sub>18</sub>N<sub>2</sub>O<sub>2</sub>S, (II), are described. The supramolecular structures of both compounds are governed by N—H···N and N—H···O hydrogen-bonding interactions. The hydrazine compound (I) shows a crystal packing with a more complex hydrogen-bonding scheme because of the NH—NH<sub>2</sub> entity, forming a di-periodic supramolecular structure extending parallel to (100). Hydrazone molecules in (II) are hydrogen-bonded through N—H···O interactions, giving rise to the formation of ribbons parallel to [010]. Molecules of (I) and (II) show a different orientation of the carbohydrazide moiety likely to favor the crystal packing and thus hydrogen-bonding interactions.

## 1. Chemical context

Hydrazine-based compounds occupy a prominent position in chemistry (Sandler & Karo, 1992) because of their pharmaceutical uses (Popiołek, 2021) and many other applications (Mali *et al.*, 2021; Koz'minykh, 2006). Their increasing importance originates from anti-inflammatory (Todeschini *et al.*, 1998), antibacterial–antifungal (Vicini *et al.*, 2002), and antitubercular (Bedia *et al.*, 2006) properties, as well as their utilization as pesticides (Pandey *et al.*, 2020). However, it is worth noting that hydrazine-based compounds applied as rocket fuels pose significant health risks owing to their toxicity (Sinha & Mason, 2014). In addition, hydrazine-based compounds function as ligand precursors for the formation of bidentate Schiff base ligands applied in metal coordination (Banna *et al.*, 2022; Zhou *et al.*, 2006; Alagesan *et al.*, 2013; Chen *et al.*, 2022).

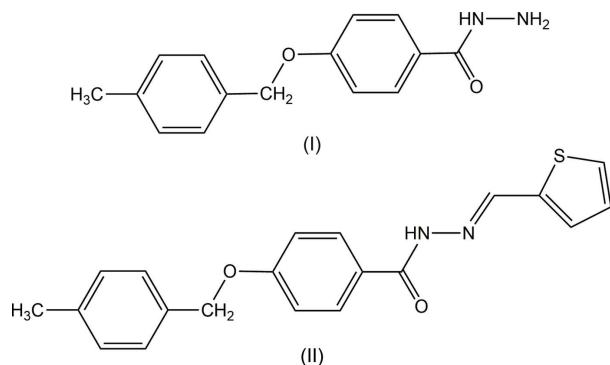
In the context given above, we report on syntheses and crystal-structure determinations of two related compounds, *viz.* a benzoylhydrazine bearing an ether group (I), C<sub>15</sub>H<sub>16</sub>N<sub>2</sub>O<sub>2</sub>, and the corresponding *N'*-[(thiophen-2-yl)methylidene] derivative (II), C<sub>20</sub>H<sub>18</sub>N<sub>2</sub>O<sub>2</sub>S.



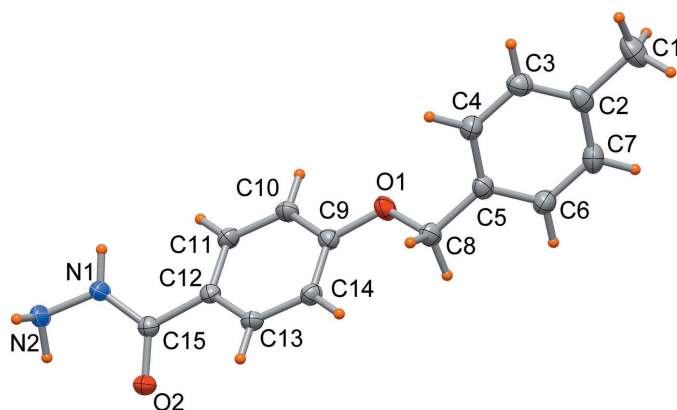
## 2. Structural commentary

The molecular structure of hydrazine compound (I) is shown in Fig. 1. The N1—N2 and the O2=C15 bond lengths of 1.4200 (15) and 1.2388 (15) Å are indicative of a single and

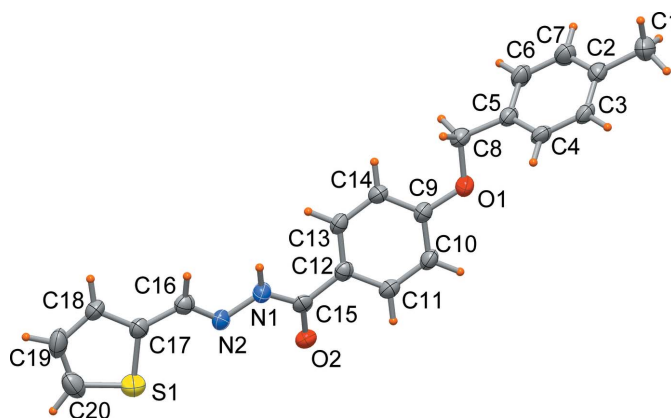
double bond, respectively. All other bond lengths are as expected when compared with molecules of similar hydrazine and hydrazone compounds (Wang, Zhou *et al.*, 2014; Wang, He *et al.*, 2014; Fun *et al.*, 2012; Zong & Wu, 2013). The conformation of the molecule shows the central phenyl ring (C9–C14) of the benzoyl mean plane forming a dihedral angle of  $66.39(3)^\circ$  with the 4-methylbenzyl group (C1–C8), and it is also rotated slightly [by  $28.49(6)^\circ$ ] with respect to the mean plane through the C=O–NH–NH<sub>2</sub> moiety.



The molecular structure of hydrazone derivative (II) is shown in Fig. 2. The thienyl (C17–C20, S1) ring and the central phenyl ring (C9–C14) are linked by the acyl–hydrazone (–CH=N–N–CO–) group. An *E*-configuration is observed with respect to the double bond of the hydrazone bridge N2=C16. Compared to (I), the N1–N2 bond length of 1.397(4) Å appears slightly shorter, most probably caused by a different intermolecular hydrogen-bonding interaction. On the other hand, the O2=C15 bond of 1.236(4) Å, is nearly identical with that of (I) and is typical for a ketonic linkage in the solid state, while an equilibrium between the keto and enol form is present in solution. The molecule has the thienyl-methylene and the benzohydrazone fragments almost coplanar, with maximum deviations of  $-0.234(3)$  and  $+0.392(2)$  Å exhibited by atoms C10 and O2, respectively. The terminal 4-methylbenzyl group is rotated by  $55.87(9)^\circ$  with respect to the central phenyl ring, similar to the dihedral angle observed in (I).



**Figure 1**  
Molecular structure of (I), with displacement ellipsoids drawn at the 50% probability level.



**Figure 2**  
Molecular structure of (II), with displacement ellipsoids drawn at the 50% probability level.

A superimposition of the two molecules (shown in Fig. 3) highlights their conformational differences: while the 4-[(4-methylbenzyl)oxy] benzoyl groups almost overlap, it is worthy to note the different orientation of the carbohydrazone C=O–NH–N moieties, likely induced by crystal packing effects to favor hydrogen-bonding interactions.

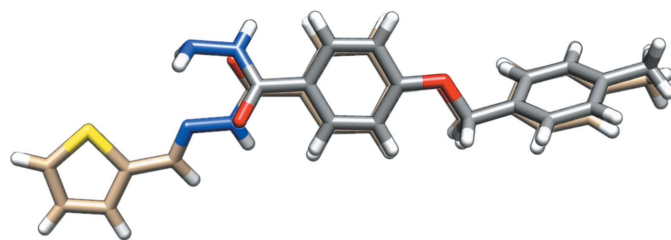
### 3. Supramolecular features

Classical hydrogen-bonding interactions represent the main contributions to the packing of the molecules in the crystals of (I) and (II); numerical data are compiled in Tables 1 and 2, respectively.

In (I), these interactions are larger because of the higher number of donor hydrogen atoms in the NH–NH<sub>2</sub> group. Fig. 4 shows the N1–H1···O2<sup>i</sup> and N2–H2B···N2<sup>iii</sup> interactions [symmetry codes: (i)  $x, y + 1, z$ ; (iii)  $-x + 1, y - \frac{1}{2}, -z - \frac{1}{2}$ ] connecting rows of oppositely oriented molecules. In addition, N2–H2A···N2<sup>iii</sup> interactions connect the rows into a layer structure extending parallel to (100) (Fig. 5).

In (II), the number of conventional hydrogen bonds is considerably reduced. The corresponding N1–H1N···O2<sup>i</sup> [symmetry code: (i)  $-x + \frac{1}{2}, y - \frac{1}{2}, z$ ] interactions create an undulating ribbon parallel to [010], as displayed in Fig. 6.

While  $\pi$  stacking interactions in (I) and (II) are insignificant, C–H··· $\pi$ -ring interactions contribute to the packing in



**Figure 3**  
Overlay plot of molecules (I) and (II) to show the conformational difference.

**Table 1**

Hydrogen-bond geometry (Å, °) for (I).

Cg1 and Cg2 are the centroids of the C2–C7 and C9–C14 rings, respectively.

D–H...A	D–H	H...A	D...A	D–H...A
N1–H1...O2 <sup>i</sup>	0.872 (18)	2.228 (18)	2.9994 (14)	147.3 (14)
N2–H2A...O2 <sup>ii</sup>	0.888 (2)	2.21 (2)	3.0598 (17)	160 (2)
N2–H2B...N2 <sup>iii</sup>	0.94 (2)	2.27 (2)	3.1970 (14)	167 (1)
C3–H3...Cg1 <sup>iv</sup>	0.95	2.86	3.6085 (16)	136
C6–H6...Cg1 <sup>v</sup>	0.95	2.83	3.5688 (16)	135
C11–H11...Cg2 <sup>vi</sup>	0.95	2.90	3.5918 (13)	131
C14–H14...Cg2 <sup>vii</sup>	0.95	2.92	3.6262 (13)	132

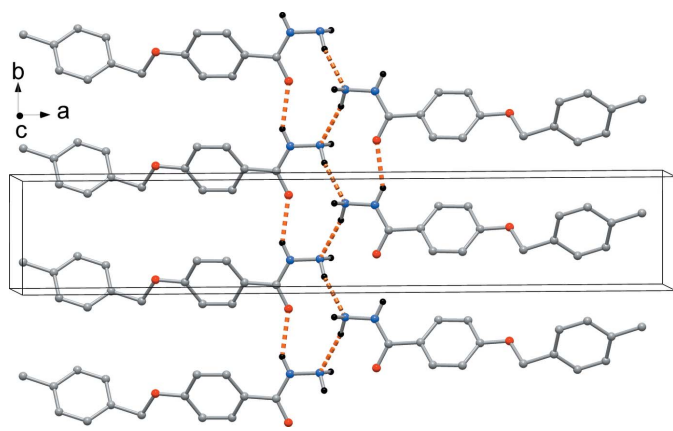
Symmetry codes: (i)  $x, y + 1, z$ ; (ii)  $-x + 1, -y + 1, -z$ ; (iii)  $-x + 1, y - \frac{1}{2}, -z - \frac{1}{2}$ ; (iv)  $x, -y + \frac{3}{2}, z + \frac{1}{2}$ ; (v)  $x, -y + \frac{1}{2}, z - \frac{1}{2}$ ; (vi)  $x, -y + \frac{3}{2}, z - \frac{1}{2}$ ; (vii)  $x, -y + \frac{1}{2}, z + \frac{1}{2}$ .

both crystals. These involve the C3–H, C6–H, and C14–H groups with phenyl rings (C2–C7; Cg1) and (C9–C14; Cg2) in (I) and (II), and the thiophene ring (Cg3) in (II). All the H...centroid distances are between 2.77–2.90 Å, with C–H... $\pi$  angles of 122–156° (Tables 1 and 2). In (II), additional C–H...O and C–H...S interactions are observed (Table 2).

#### 4. Synthesis and crystallization

**Synthesis of compound (I).** A mixture of ethyl-4-[(4-methylbenzyl)oxy] benzoate (1.23 g, 4.55 mmol) and hydrazine hydrate (5.83 g, 22.69 mmol) in absolute ethanol (20 ml) was refluxed for 10 h. After cooling the solution to room temperature, colorless crystals, suitable for X-ray diffraction, were obtained. Yield: 0.82 g, 70%; melting point: 397–398 K;

FT-IR: 1644  $\nu$  (C=O<sub>amide</sub>), 3374  $\nu$  (N–H); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz):  $\delta$  = 2.36 (*s*, 3H, –CH<sub>3</sub>), 4.05 (*brs*, 2H, –NH<sub>2</sub>), 5.07 (*s*, 2H, –CH<sub>2</sub>–), 6.99 (*d*, 2H, Ar-H 5,6, *J* = 13.2 Hz), 7.20 (*d*, 2H, Ar-H 10,11, *J* = 11.4 Hz), 7.30 (*d*, 2H, Ar-H 8,9, *J* = 12 Hz), 7.70 (*d*, 2H, Ar-H 3,4, *J* = 10.2 Hz), ppm; <sup>13</sup>C NMR (CDCl<sub>3</sub>, 600 MHz): 21.3 (C7), 70.1 (C8), 114.8 (C-3,5), 125.08 (C1), 127.73 (C-2',6'), 128.7 (C-2,6), 129.4 (C-3',5'), 133.2 (C1), 138.13 (C4), 161.7 (C4), 168.4 (C9) ppm; LC-MS (ESI) *m/z*: [*M* + H]<sup>+</sup>. Calculated for C<sub>15</sub>H<sub>16</sub>N<sub>2</sub>O<sub>2</sub>; 257.1283;



**Figure 4**

The rows built by N–H...N and N–H...O interactions (orange dashed lines) in the crystal structure of (I).

**Table 2**

Hydrogen-bond geometry (Å, °) for (II).

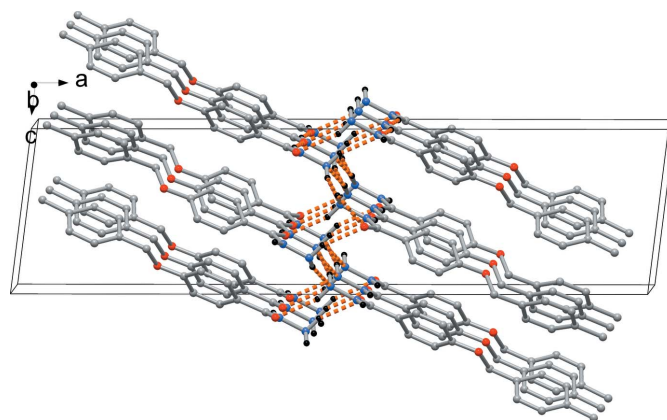
Cg1, Cg2 and Cg3 are the centroids of the C2–C7, C9–C14 and thiophene rings, respectively.

D–H...A	D–H	H...A	D...A	D–H...A
N1–H1N...O2 <sup>i</sup>	0.87 (4)	2.04 (4)	2.899 (4)	170 (4)
C10–H10...O1 <sup>ii</sup>	0.95	2.62	3.409 (4)	140
C16–H16...O2 <sup>i</sup>	0.95	2.49	3.316 (5)	146
C18–H18...S1 <sup>iii</sup>	0.95	3.00	3.938 (4)	170
C19–H19...O2 <sup>iv</sup>	0.95	2.65	3.319 (5)	128
C19–H19...O2 <sup>iv</sup>	0.95	2.65	3.319 (5)	128
C3–H3...Cg2 <sup>v</sup>	0.95	2.77	3.540 (4)	138
C6–H6...Cg1 <sup>vi</sup>	0.95	2.80	3.593 (4)	141
C14–H14...Cg2 <sup>i</sup>	0.95	2.90	3.504 (4)	122
C18–H18...Cg3 <sup>iii</sup>	0.95	2.92	3.803 (4)	156

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

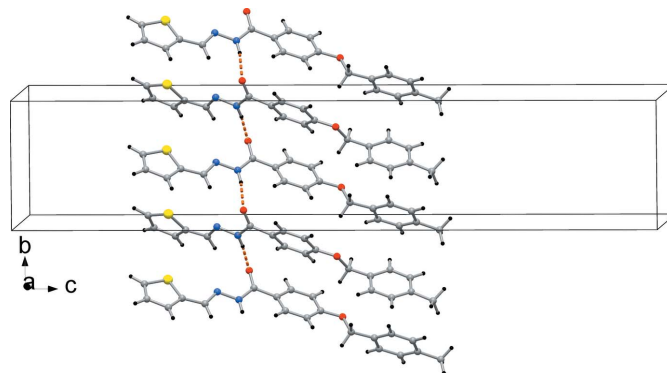
found 257.1284. The proton at the NH group was missing, likely due to the exchangeable nature of this proton.

**Synthesis of compound (II).** Thiophene-2-carbaldehyde (0.15 g, 1.21 mmol) was added to an absolute ethanolic (20 ml) solution of 4-[(4-methylbenzyl)oxy]benzoylhydrazine (0.312 g, 1.21 mmol). The resulting mixture was heated and refluxed for



**Figure 5**

The layered arrangement in the crystal packing of (I) caused by additional N–H...O interactions.



**Figure 6**

The chain structure in the crystal packing of (II) with indication of N–H...O hydrogen bonds (orange dashed lines).

**Table 3**  
Experimental details.

	(I)	(II)
<b>Crystal data</b>		
Chemical formula	C <sub>15</sub> H <sub>16</sub> N <sub>2</sub> O <sub>2</sub>	C <sub>20</sub> H <sub>18</sub> N <sub>2</sub> O <sub>2</sub> S
<i>M<sub>r</sub></i>	256.30	350.42
Crystal system, space group	Monoclinic, <i>P2<sub>1</sub>/c</i>	Orthorhombic, <i>Pbca</i>
Temperature (K)	173	173
<i>a</i> , <i>b</i> , <i>c</i> (Å)	30.7086 (14), 5.2471 (3), 8.0359 (4)	11.3725 (8), 7.8492 (5), 39.286 (2)
$\alpha$ , $\beta$ , $\gamma$ (°)	90, 97.471 (7), 90	90, 90, 90
<i>V</i> (Å <sup>3</sup> )	1283.85 (11)	3506.8 (4)
<i>Z</i>	4	8
Radiation type	Mo <i>K</i> $\alpha$	Mo <i>K</i> $\alpha$
$\mu$ (mm <sup>-1</sup> )	0.09	0.20
Crystal size (mm)	0.17 × 0.16 × 0.13	0.26 × 0.08 × 0.01
<b>Data collection</b>		
Diffractometer	Rigaku R-Axis RAPID	Rigaku R-Axis RAPID
Absorption correction	Multi-scan ( <i>ABSCOR</i> ; Higashi, 1995)	Multi-scan ( <i>ABSCOR</i> ; Higashi, 1995)
<i>T<sub>min</sub></i> , <i>T<sub>max</sub></i>	0.739, 0.988	0.646, 0.998
No. of measured, independent and observed [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )] reflections	9727, 2889, 2515	31564, 4006, 2203
<i>R<sub>int</sub></i>	0.024	0.162
( <i>sin</i> $\theta$ / $\lambda$ ) <sub>max</sub> (Å <sup>-1</sup> )	0.648	0.649
<b>Refinement</b>		
<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>	0.044, 0.126, 1.04	0.078, 0.201, 1.02
No. of reflections	2889	4006
No. of parameters	182	230
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\max}$ , $\Delta\rho_{\min}$ (e Å <sup>-3</sup> )	0.36, -0.25	0.28, -0.46

Computer programs: *RAPID-AUTO* (Rigaku, 2018), *SHELXT* (Sheldrick, 2015a), *SHELXL* (Sheldrick, 2015b), *DIAMOND* (Brandenburg, 1999) and *WinGX* publication routines (Farrugia, 2012).

2 h. A white precipitate was obtained, filtered off, and washed several times with hot ethanol, and finally dried over silica gel in a desiccator. A small amount of the compound was dissolved in 25 ml of absolute ethanol and allowed for slow evaporation. Suitable crystals for single-crystal X-ray diffraction were collected after 30 d of keeping the sample solution undisturbed. Yield: 0.86 g, 50%; melting point: 505–506 K.

FT-IR: 1634  $\nu$  (C=O<sub>amide</sub>), 3204  $\nu$  (N-H), 1607 (C=N<sub>azomethine</sub>); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz):  $\delta$  = 2.36 (*s*, 3H, -CH<sub>3</sub>), 5.07 (*s*, 2H, -CH<sub>2</sub>-), 7.03 (*d*, 2H, Ar-H 5,6, *J* = 13.2 Hz), 7.20 (*d*, 2H, Ar-H 10,11, *J* = 11.4 Hz), 7.32 (*d*, 2H, Ar-H 8,9, *J* = 12 Hz), 7.39–7.40 (*m*, 1H, CH=N), 8.9 (*s*, 1H, -CONH-) ppm; LC-MS (ESI) *m/z*: [*M* + H]<sup>+</sup>. Calculated for C<sub>20</sub>H<sub>18</sub>N<sub>2</sub>O<sub>2</sub>S; 351.1159; found 351.1162.

We failed to locate the <sup>1</sup>H NMR signals of Ar-H 3,4 and of thiophene ring hydrogen atoms, likely due to the poor solubility of the compound in organic solvents.

## 5. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. Hydrogen atoms were calculated at geometrical positions and refined as riding [C–H = 0.95–0.99 Å, *U*<sub>iso</sub>(H) = 1.2*U*<sub>eq</sub>(C)], except those of the –NH–NH<sub>2</sub> (I) and –NH–N= (II) groups, which were detected in difference-Fourier maps and freely refined.

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## supporting information

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## Crystal structures of 4-[(4-methylbenzyl)oxy]benzohydrazide and its *N'*-[(thiophen-2-yl)methylidene]- derivative

**Md. Hasan Al Banna, Md. Belayet Hossain Howlader, Ryuta Miyatake, Md. Chanmiya Sheikh, Md. Rezaul Haque Ansary and Ennio Zangrando**

### Computing details

For both structures, data collection: *RAPID-AUTO* (Rigaku, 2018); cell refinement: *RAPID-AUTO* (Rigaku, 2018); data reduction: *RAPID-AUTO* (Rigaku, 2018). Program(s) used to solve structure: *SHELXT2018/2* (Sheldrick, 2015a) for (I); *SHELXT* (Sheldrick, 2015a) for (II). For both structures, program(s) used to refine structure: *SHELXL2019/2* (Sheldrick, 2015b); molecular graphics: *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *WinGX* publication routines (Farrugia, 2012).

### 4-[(4-Methylbenzyl)oxy]benzohydrazide (I)

#### Crystal data

$C_{15}H_{16}N_2O_2$

$M_r = 256.30$

Monoclinic,  $P2_1/c$

$a = 30.7086$  (14) Å

$b = 5.2471$  (3) Å

$c = 8.0359$  (4) Å

$\beta = 97.471$  (7)°

$V = 1283.85$  (11) Å<sup>3</sup>

$Z = 4$

$F(000) = 544$

$D_x = 1.326$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation,  $\lambda = 0.71075$  Å

Cell parameters from 8347 reflections

$\theta = 2.0$ – $27.4$ °

$\mu = 0.09$  mm<sup>-1</sup>

$T = 173$  K

Prism, colorless

$0.17 \times 0.16 \times 0.13$  mm

#### Data collection

Rigaku R-AXIS RAPID

diffractometer

Detector resolution: 10.000 pixels mm<sup>-1</sup>

$\omega$  scans

Absorption correction: multi-scan

(ABSCOR; Higashi, 1995)

$T_{\min} = 0.739$ ,  $T_{\max} = 0.988$

9727 measured reflections

2889 independent reflections

2515 reflections with  $I > 2\sigma(I)$

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

$\theta_{\max} = 27.4$ °,  $\theta_{\min} = 2.7$ °

$h = -39 \rightarrow 39$

$k = -6 \rightarrow 6$

$l = -7 \rightarrow 10$

#### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.044$

$wR(F^2) = 0.126$

$S = 1.04$

2889 reflections

182 parameters

0 restraints

Hydrogen site location: mixed

H atoms treated by a mixture of independent and constrained refinement



$$w = 1/[\sigma^2(F_o^2) + (0.0685P)^2 + 0.437P]$$

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

$$\Delta\rho_{\max} = 0.36 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.25 \text{ e } \text{\AA}^{-3}$$

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
O1	0.76070 (3)	0.52411 (17)	0.25819 (12)	0.0286 (2)
O2	0.56320 (3)	0.27730 (17)	-0.03945 (13)	0.0313 (2)
N1	0.56104 (3)	0.7071 (2)	-0.06599 (15)	0.0269 (3)
H1	0.5729 (5)	0.857 (3)	-0.046 (2)	0.032*
N2	0.51729 (4)	0.7187 (2)	-0.14851 (18)	0.0314 (3)
H2a	0.4990 (6)	0.724 (3)	-0.072 (3)	0.038*
H2b	0.5119 (6)	0.568 (4)	-0.212 (2)	0.038*
C1	0.95555 (5)	0.6618 (4)	0.6481 (2)	0.0471 (4)
H1A	0.970910	0.734626	0.559722	0.057*
H1B	0.972202	0.515957	0.699105	0.057*
H1C	0.952889	0.791252	0.734154	0.057*
C2	0.91027 (4)	0.5748 (3)	0.57322 (17)	0.0316 (3)
C3	0.87328 (5)	0.7144 (3)	0.60247 (18)	0.0317 (3)
H3	0.876869	0.864907	0.668564	0.038*
C4	0.83138 (4)	0.6368 (3)	0.53651 (18)	0.0295 (3)
H4	0.806674	0.735051	0.557333	0.035*
C5	0.82520 (4)	0.4160 (2)	0.44003 (16)	0.0253 (3)
C6	0.86196 (5)	0.2773 (3)	0.40966 (18)	0.0311 (3)
H6	0.858381	0.127510	0.342843	0.037*
C7	0.90393 (4)	0.3557 (3)	0.47622 (19)	0.0343 (3)
H7	0.928632	0.257732	0.454939	0.041*
C8	0.77962 (4)	0.3300 (2)	0.37186 (17)	0.0271 (3)
H8A	0.780838	0.165724	0.312103	0.032*
H8B	0.761665	0.306844	0.464516	0.032*
C9	0.71691 (4)	0.5041 (2)	0.19621 (15)	0.0225 (3)
C10	0.70076 (4)	0.6971 (2)	0.08495 (17)	0.0249 (3)
H10	0.719868	0.827904	0.056518	0.030*
C11	0.65699 (4)	0.6983 (2)	0.01604 (16)	0.0244 (3)
H11	0.646167	0.830898	-0.058621	0.029*
C12	0.62868 (4)	0.5054 (2)	0.05582 (15)	0.0216 (3)
C13	0.64525 (4)	0.3131 (2)	0.16527 (16)	0.0234 (3)
H13	0.626219	0.180748	0.191960	0.028*
C14	0.68913 (4)	0.3099 (2)	0.23678 (16)	0.0239 (3)
H14	0.699909	0.177669	0.311821	0.029*
C15	0.58137 (4)	0.4879 (2)	-0.01986 (16)	0.0232 (3)

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

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
O1	0.0213 (4)	0.0294 (5)	0.0335 (5)	-0.0023 (3)	-0.0020 (4)	0.0092 (4)
O2	0.0258 (5)	0.0205 (5)	0.0454 (6)	-0.0024 (3)	-0.0031 (4)	-0.0008 (4)
N1	0.0224 (5)	0.0201 (5)	0.0363 (6)	-0.0013 (4)	-0.0040 (4)	0.0005 (4)
N2	0.0222 (5)	0.0246 (6)	0.0448 (7)	0.0003 (4)	-0.0063 (5)	0.0026 (5)
C1	0.0287 (7)	0.0612 (11)	0.0487 (10)	-0.0065 (7)	-0.0055 (6)	0.0012 (8)
C2	0.0262 (6)	0.0368 (7)	0.0303 (7)	-0.0019 (5)	-0.0021 (5)	0.0065 (6)
C3	0.0335 (7)	0.0293 (7)	0.0314 (7)	-0.0032 (5)	0.0005 (5)	-0.0024 (5)
C4	0.0266 (6)	0.0286 (6)	0.0330 (7)	0.0036 (5)	0.0032 (5)	-0.0013 (5)
C5	0.0240 (6)	0.0260 (6)	0.0250 (6)	0.0006 (5)	0.0002 (5)	0.0045 (5)
C6	0.0307 (7)	0.0278 (6)	0.0339 (7)	0.0043 (5)	0.0005 (5)	-0.0019 (5)
C7	0.0249 (6)	0.0393 (7)	0.0384 (8)	0.0078 (6)	0.0028 (5)	0.0020 (6)
C8	0.0252 (6)	0.0256 (6)	0.0291 (6)	0.0003 (5)	-0.0014 (5)	0.0048 (5)
C9	0.0216 (5)	0.0228 (6)	0.0228 (6)	0.0004 (4)	0.0016 (4)	-0.0014 (4)
C10	0.0242 (6)	0.0215 (6)	0.0290 (7)	-0.0036 (4)	0.0031 (5)	0.0030 (5)
C11	0.0259 (6)	0.0200 (6)	0.0268 (6)	0.0011 (5)	0.0019 (5)	0.0035 (4)
C12	0.0217 (6)	0.0191 (5)	0.0237 (6)	0.0009 (4)	0.0018 (4)	-0.0030 (4)
C13	0.0239 (6)	0.0196 (5)	0.0266 (6)	-0.0025 (4)	0.0030 (5)	0.0006 (4)
C14	0.0259 (6)	0.0204 (6)	0.0250 (6)	0.0009 (4)	0.0015 (5)	0.0025 (4)
C15	0.0235 (6)	0.0215 (6)	0.0242 (6)	-0.0002 (4)	0.0017 (5)	-0.0007 (4)

Geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

O1—C9	1.3758 (14)	C5—C6	1.3913 (18)
O1—C8	1.4391 (15)	C5—C8	1.5043 (17)
O2—C15	1.2388 (15)	C6—C7	1.3918 (19)
N1—C15	1.3380 (15)	C6—H6	0.9500
N1—N2	1.4200 (15)	C7—H7	0.9500
N1—H1	0.872 (18)	C8—H8A	0.9900
N2—H2A	0.88 (2)	C8—H8B	0.9900
N2—H2B	0.94 (2)	C9—C14	1.3945 (17)
C1—C2	1.5123 (19)	C9—C10	1.3986 (17)
C1—H1A	0.9800	C10—C11	1.3853 (17)
C1—H1B	0.9800	C10—H10	0.9500
C1—H1C	0.9800	C11—C12	1.3982 (16)
C2—C7	1.388 (2)	C11—H11	0.9500
C2—C3	1.397 (2)	C12—C13	1.3908 (17)
C3—C4	1.3876 (18)	C12—C15	1.5031 (16)
C3—H3	0.9500	C13—C14	1.3946 (16)
C4—C5	1.3930 (18)	C13—H13	0.9500
C4—H4	0.9500	C14—H14	0.9500
C9—O1—C8	118.08 (9)	C2—C7—H7	119.5
C15—N1—N2	123.03 (10)	C6—C7—H7	119.5
C15—N1—H1	123.6 (11)	O1—C8—C5	107.39 (10)
N2—N1—H1	113.3 (11)	O1—C8—H8A	110.2



N1—N2—H2A	108.9 (12)	C5—C8—H8A	110.2
N1—N2—H2B	107.8 (10)	O1—C8—H8B	110.2
H2A—N2—H2B	108.7 (16)	C5—C8—H8B	110.2
C2—C1—H1A	109.5	H8A—C8—H8B	108.5
C2—C1—H1B	109.5	O1—C9—C14	124.75 (11)
H1A—C1—H1B	109.5	O1—C9—C10	115.14 (10)
C2—C1—H1C	109.5	C14—C9—C10	120.11 (11)
H1A—C1—H1C	109.5	C11—C10—C9	120.26 (11)
H1B—C1—H1C	109.5	C11—C10—H10	119.9
C7—C2—C3	118.10 (12)	C9—C10—H10	119.9
C7—C2—C1	121.88 (13)	C10—C11—C12	120.33 (11)
C3—C2—C1	120.02 (14)	C10—C11—H11	119.8
C4—C3—C2	121.04 (13)	C12—C11—H11	119.8
C4—C3—H3	119.5	C13—C12—C11	118.86 (11)
C2—C3—H3	119.5	C13—C12—C15	117.80 (10)
C3—C4—C5	120.61 (12)	C11—C12—C15	123.28 (11)
C3—C4—H4	119.7	C12—C13—C14	121.59 (11)
C5—C4—H4	119.7	C12—C13—H13	119.2
C6—C5—C4	118.54 (12)	C14—C13—H13	119.2
C6—C5—C8	121.12 (12)	C13—C14—C9	118.85 (11)
C4—C5—C8	120.33 (11)	C13—C14—H14	120.6
C5—C6—C7	120.65 (13)	C9—C14—H14	120.6
C5—C6—H6	119.7	O2—C15—N1	123.06 (11)
C7—C6—H6	119.7	O2—C15—C12	120.11 (10)
C2—C7—C6	121.05 (12)	N1—C15—C12	116.83 (10)
C7—C2—C3—C4	0.0 (2)	C14—C9—C10—C11	0.79 (19)
C1—C2—C3—C4	-179.31 (14)	C9—C10—C11—C12	-0.60 (19)
C2—C3—C4—C5	0.4 (2)	C10—C11—C12—C13	-0.06 (18)
C3—C4—C5—C6	-0.8 (2)	C10—C11—C12—C15	-177.22 (11)
C3—C4—C5—C8	178.74 (12)	C11—C12—C13—C14	0.55 (18)
C4—C5—C6—C7	0.9 (2)	C15—C12—C13—C14	177.86 (11)
C8—C5—C6—C7	-178.67 (13)	C12—C13—C14—C9	-0.36 (18)
C3—C2—C7—C6	0.1 (2)	O1—C9—C14—C13	179.74 (11)
C1—C2—C7—C6	179.37 (14)	C10—C9—C14—C13	-0.31 (18)
C5—C6—C7—C2	-0.5 (2)	N2—N1—C15—O2	-2.9 (2)
C9—O1—C8—C5	-171.75 (10)	N2—N1—C15—C12	175.97 (12)
C6—C5—C8—O1	-117.28 (13)	C13—C12—C15—O2	-27.44 (17)
C4—C5—C8—O1	63.20 (16)	C11—C12—C15—O2	149.75 (13)
C8—O1—C9—C14	0.69 (18)	C13—C12—C15—N1	153.70 (12)
C8—O1—C9—C10	-179.27 (11)	C11—C12—C15—N1	-29.12 (17)
O1—C9—C10—C11	-179.25 (11)		

*Hydrogen-bond geometry (Å, °)*

*Cg*1 and *Cg*2 are the centroids of the C2–C7 and C9–C14 rings, respectively.

<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>
N1—H1...O2 <sup>i</sup>	0.872 (18)	2.228 (18)	2.9994 (14)	147.3 (14)

N2—H2A...O2 <sup>ii</sup>	0.88 (2)	2.21 (2)	3.0598 (17)	160 (2)
N2—H2B...N2 <sup>iii</sup>	0.94 (2)	2.27 (2)	3.1970 (14)	167 (1)
C3—H3...Cg1 <sup>iv</sup>	0.95	2.86	3.6085 (16)	136
C6—H6...Cg1 <sup>v</sup>	0.95	2.83	3.5688 (16)	135
C11—H11...Cg2 <sup>vi</sup>	0.95	2.90	3.5918 (13)	131
C14—H14...Cg2 <sup>vii</sup>	0.95	2.92	3.6262 (13)	132

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

#### 4-[(4-Methylbenzyl)oxy]-*N'*-[(thiophen-2-yl)methylidene]benzohydrazide (II)

##### Crystal data

$C_{20}H_{18}N_2O_2S$

$M_r = 350.42$

Orthorhombic, *Pbca*

$a = 11.3725$  (8) Å

$b = 7.8492$  (5) Å

$c = 39.286$  (2) Å

$V = 3506.8$  (4) Å<sup>3</sup>

$Z = 8$

$F(000) = 1472$

$D_x = 1.327$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation,  $\lambda = 0.71075$  Å

Cell parameters from 12507 reflections

$\theta = 1.9$ – $27.4^\circ$

$\mu = 0.20$  mm<sup>-1</sup>

$T = 173$  K

Plate, colorless

$0.26 \times 0.08 \times 0.01$  mm

##### Data collection

Rigaku R-AXIS RAPID

diffractometer

Detector resolution: 10.000 pixels mm<sup>-1</sup>

$\omega$  scans

Absorption correction: multi-scan

(ABSCOR; Higashi, 1995)

$T_{\min} = 0.646$ ,  $T_{\max} = 0.998$

31564 measured reflections

4006 independent reflections

2203 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.162$

$\theta_{\max} = 27.5^\circ$ ,  $\theta_{\min} = 2.1^\circ$

$h = -14 \rightarrow 14$

$k = -10 \rightarrow 10$

$l = -50 \rightarrow 50$

##### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.078$

$wR(F^2) = 0.201$

$S = 1.02$

4006 reflections

230 parameters

0 restraints

Hydrogen site location: mixed

H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0867P)^2 + 2.4194P]$

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

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

$\Delta\rho_{\max} = 0.28$  e Å<sup>-3</sup>

$\Delta\rho_{\min} = -0.46$  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 (Å<sup>2</sup>)

	$x$	$y$	$z$	$U_{\text{iso}}^*/U_{\text{eq}}$
S1	0.22046 (10)	0.59338 (16)	0.23512 (3)	0.0543 (3)
O1	0.3869 (2)	0.2842 (3)	0.50032 (6)	0.0403 (7)

O2	0.3905 (2)	0.6420 (3)	0.35634 (6)	0.0364 (6)
N1	0.2605 (3)	0.4326 (4)	0.34359 (8)	0.0384 (8)
H1N	0.220 (4)	0.343 (5)	0.3497 (10)	0.046*
N2	0.2419 (3)	0.4962 (4)	0.31082 (7)	0.0361 (7)
C1	0.4445 (4)	-0.0531 (6)	0.65013 (10)	0.0586 (12)
H1A	0.432854	0.036538	0.667172	0.070*
H1B	0.527637	-0.085807	0.649593	0.070*
H1C	0.396550	-0.152458	0.656079	0.070*
C2	0.4081 (3)	0.0126 (5)	0.61544 (9)	0.0399 (9)
C3	0.4761 (3)	-0.0238 (5)	0.58686 (9)	0.0387 (9)
H3	0.546925	-0.086739	0.589404	0.046*
C4	0.4420 (3)	0.0303 (5)	0.55480 (10)	0.0380 (9)
H4	0.488311	0.001132	0.535548	0.046*
C5	0.3407 (3)	0.1269 (5)	0.55051 (9)	0.0355 (9)
C6	0.2739 (3)	0.1669 (5)	0.57909 (9)	0.0428 (10)
H6	0.204834	0.233913	0.576795	0.051*
C7	0.3084 (3)	0.1088 (6)	0.61105 (10)	0.0482 (11)
H7	0.261670	0.136347	0.630331	0.058*
C8	0.2990 (3)	0.1780 (5)	0.51590 (9)	0.0391 (9)
H8A	0.285445	0.075437	0.501774	0.047*
H8B	0.223934	0.241183	0.517765	0.047*
C9	0.3674 (3)	0.3338 (5)	0.46694 (9)	0.0345 (8)
C10	0.4558 (3)	0.4314 (5)	0.45250 (9)	0.0369 (9)
H10	0.523935	0.459873	0.465289	0.044*
C11	0.4438 (3)	0.4872 (5)	0.41914 (9)	0.0351 (8)
H11	0.503537	0.555552	0.409199	0.042*
C12	0.3447 (3)	0.4438 (4)	0.40007 (9)	0.0318 (8)
C13	0.2571 (3)	0.3477 (5)	0.41541 (9)	0.0334 (8)
H13	0.188522	0.319851	0.402784	0.040*
C14	0.2673 (3)	0.2915 (4)	0.44869 (9)	0.0337 (8)
H14	0.206828	0.225189	0.458814	0.040*
C15	0.3346 (3)	0.5139 (5)	0.36493 (9)	0.0321 (8)
C16	0.1662 (3)	0.4133 (5)	0.29375 (9)	0.0372 (9)
H16	0.128409	0.318128	0.303940	0.045*
C17	0.1361 (3)	0.4599 (5)	0.25919 (9)	0.0380 (9)
C18	0.0398 (3)	0.4010 (5)	0.24049 (9)	0.0402 (9)
H18	-0.018133	0.325460	0.249223	0.048*
C19	0.0387 (4)	0.4664 (6)	0.20742 (11)	0.0597 (13)
H19	-0.019933	0.439397	0.191077	0.072*
C20	0.1296 (4)	0.5718 (7)	0.20114 (11)	0.0602 (13)
H20	0.141558	0.627988	0.179994	0.072*

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

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
S1	0.0499 (7)	0.0616 (7)	0.0514 (7)	-0.0076 (6)	0.0008 (5)	0.0057 (6)
O1	0.0346 (15)	0.0494 (16)	0.0369 (14)	-0.0071 (12)	-0.0077 (11)	0.0036 (13)
O2	0.0283 (13)	0.0410 (14)	0.0400 (15)	-0.0030 (12)	0.0020 (11)	0.0010 (12)

N1	0.0334 (18)	0.0432 (19)	0.0384 (18)	-0.0054 (15)	-0.0072 (14)	0.0057 (16)
N2	0.0288 (16)	0.0430 (17)	0.0365 (16)	0.0033 (14)	-0.0040 (13)	0.0031 (15)
C1	0.046 (3)	0.082 (3)	0.048 (3)	-0.003 (2)	-0.009 (2)	0.016 (2)
C2	0.032 (2)	0.046 (2)	0.042 (2)	-0.0084 (18)	-0.0063 (16)	0.0045 (19)
C3	0.0222 (18)	0.044 (2)	0.050 (2)	-0.0003 (16)	-0.0057 (16)	0.0036 (19)
C4	0.0222 (18)	0.047 (2)	0.045 (2)	-0.0016 (17)	0.0027 (16)	-0.0018 (18)
C5	0.0261 (18)	0.039 (2)	0.041 (2)	-0.0020 (16)	-0.0036 (16)	0.0047 (18)
C6	0.026 (2)	0.055 (2)	0.047 (2)	0.0075 (18)	-0.0027 (16)	-0.004 (2)
C7	0.033 (2)	0.069 (3)	0.043 (2)	0.005 (2)	0.0003 (17)	-0.004 (2)
C8	0.030 (2)	0.044 (2)	0.043 (2)	-0.0070 (17)	-0.0024 (16)	0.0029 (19)
C9	0.027 (2)	0.039 (2)	0.038 (2)	0.0007 (15)	-0.0028 (15)	0.0005 (17)
C10	0.0260 (19)	0.044 (2)	0.041 (2)	-0.0024 (16)	-0.0056 (15)	-0.0027 (18)
C11	0.0263 (19)	0.037 (2)	0.042 (2)	-0.0003 (16)	0.0008 (15)	0.0000 (17)
C12	0.0254 (18)	0.034 (2)	0.036 (2)	0.0053 (15)	0.0001 (14)	-0.0019 (16)
C13	0.0244 (18)	0.0373 (19)	0.039 (2)	0.0027 (15)	-0.0039 (15)	-0.0037 (17)
C14	0.0267 (19)	0.038 (2)	0.0365 (19)	-0.0033 (16)	0.0010 (15)	0.0003 (17)
C15	0.0223 (18)	0.038 (2)	0.036 (2)	0.0077 (16)	0.0047 (14)	-0.0011 (17)
C16	0.030 (2)	0.039 (2)	0.042 (2)	0.0035 (17)	-0.0002 (16)	0.0043 (18)
C17	0.030 (2)	0.045 (2)	0.038 (2)	0.0058 (17)	-0.0012 (15)	0.0025 (18)
C18	0.0267 (19)	0.053 (2)	0.041 (2)	-0.0067 (18)	-0.0040 (15)	0.0010 (19)
C19	0.044 (3)	0.082 (3)	0.054 (3)	0.013 (3)	-0.020 (2)	-0.004 (3)
C20	0.066 (3)	0.074 (3)	0.040 (2)	0.014 (3)	-0.001 (2)	0.010 (2)

*Geometric parameters (Å, °)*

S1—C20	1.697 (5)	C7—H7	0.9500
S1—C17	1.707 (4)	C8—H8A	0.9900
O1—C9	1.386 (4)	C8—H8B	0.9900
O1—C8	1.438 (4)	C9—C14	1.386 (5)
O2—C15	1.236 (4)	C9—C10	1.386 (5)
N1—C15	1.349 (5)	C10—C11	1.389 (5)
N1—N2	1.397 (4)	C10—H10	0.9500
N1—H1N	0.87 (4)	C11—C12	1.395 (5)
N2—C16	1.271 (5)	C11—H11	0.9500
C1—C2	1.515 (5)	C12—C13	1.387 (5)
C1—H1A	0.9800	C12—C15	1.491 (5)
C1—H1B	0.9800	C13—C14	1.385 (5)
C1—H1C	0.9800	C13—H13	0.9500
C2—C7	1.373 (5)	C14—H14	0.9500
C2—C3	1.393 (5)	C16—C17	1.447 (5)
C3—C4	1.385 (5)	C16—H16	0.9500
C3—H3	0.9500	C17—C18	1.398 (5)
C4—C5	1.389 (5)	C18—C19	1.397 (6)
C4—H4	0.9500	C18—H18	0.9500
C5—C6	1.391 (5)	C19—C20	1.347 (7)
C5—C8	1.495 (5)	C19—H19	0.9500
C6—C7	1.392 (5)	C20—H20	0.9500
C6—H6	0.9500		

C20—S1—C17	91.9 (2)	C14—C9—C10	121.1 (3)
C9—O1—C8	117.0 (3)	C14—C9—O1	123.6 (3)
C15—N1—N2	119.9 (3)	C10—C9—O1	115.3 (3)
C15—N1—H1N	122 (3)	C9—C10—C11	119.3 (3)
N2—N1—H1N	118 (3)	C9—C10—H10	120.4
C16—N2—N1	114.0 (3)	C11—C10—H10	120.4
C2—C1—H1A	109.5	C10—C11—C12	120.6 (3)
C2—C1—H1B	109.5	C10—C11—H11	119.7
H1A—C1—H1B	109.5	C12—C11—H11	119.7
C2—C1—H1C	109.5	C13—C12—C11	118.7 (3)
H1A—C1—H1C	109.5	C13—C12—C15	123.2 (3)
H1B—C1—H1C	109.5	C11—C12—C15	118.0 (3)
C7—C2—C3	118.1 (3)	C14—C13—C12	121.6 (3)
C7—C2—C1	121.7 (4)	C14—C13—H13	119.2
C3—C2—C1	120.2 (4)	C12—C13—H13	119.2
C4—C3—C2	121.0 (3)	C13—C14—C9	118.8 (3)
C4—C3—H3	119.5	C13—C14—H14	120.6
C2—C3—H3	119.5	C9—C14—H14	120.6
C3—C4—C5	120.7 (3)	O2—C15—N1	122.4 (3)
C3—C4—H4	119.7	O2—C15—C12	120.9 (3)
C5—C4—H4	119.7	N1—C15—C12	116.7 (3)
C4—C5—C6	118.5 (3)	N2—C16—C17	121.7 (4)
C4—C5—C8	121.3 (3)	N2—C16—H16	119.1
C6—C5—C8	120.0 (3)	C17—C16—H16	119.1
C5—C6—C7	120.0 (4)	C18—C17—C16	126.5 (4)
C5—C6—H6	120.0	C18—C17—S1	110.6 (3)
C7—C6—H6	120.0	C16—C17—S1	122.8 (3)
C2—C7—C6	121.7 (4)	C19—C18—C17	111.9 (4)
C2—C7—H7	119.1	C19—C18—H18	124.0
C6—C7—H7	119.1	C17—C18—H18	124.0
O1—C8—C5	108.8 (3)	C20—C19—C18	113.0 (4)
O1—C8—H8A	109.9	C20—C19—H19	123.5
C5—C8—H8A	109.9	C18—C19—H19	123.5
O1—C8—H8B	109.9	C19—C20—S1	112.6 (3)
C5—C8—H8B	109.9	C19—C20—H20	123.7
H8A—C8—H8B	108.3	S1—C20—H20	123.7
C15—N1—N2—C16	-176.9 (3)	C11—C12—C13—C14	-1.5 (5)
C7—C2—C3—C4	-2.2 (6)	C15—C12—C13—C14	-176.9 (3)
C1—C2—C3—C4	177.8 (4)	C12—C13—C14—C9	0.4 (5)
C2—C3—C4—C5	1.9 (6)	C10—C9—C14—C13	0.5 (5)
C3—C4—C5—C6	-0.4 (5)	O1—C9—C14—C13	-179.9 (3)
C3—C4—C5—C8	-176.5 (3)	N2—N1—C15—O2	-2.1 (5)
C4—C5—C6—C7	-0.7 (6)	N2—N1—C15—C12	176.6 (3)
C8—C5—C6—C7	175.4 (4)	C13—C12—C15—O2	154.6 (3)
C3—C2—C7—C6	1.0 (6)	C11—C12—C15—O2	-20.9 (5)
C1—C2—C7—C6	-179.0 (4)	C13—C12—C15—N1	-24.2 (5)

C5—C6—C7—C2	0.5 (6)	C11—C12—C15—N1	160.3 (3)
C9—O1—C8—C5	175.3 (3)	N1—N2—C16—C17	-179.5 (3)
C4—C5—C8—O1	-62.3 (5)	N2—C16—C17—C18	-166.6 (4)
C6—C5—C8—O1	121.7 (4)	N2—C16—C17—S1	15.7 (5)
C8—O1—C9—C14	2.3 (5)	C20—S1—C17—C18	0.2 (3)
C8—O1—C9—C10	-178.1 (3)	C20—S1—C17—C16	178.2 (3)
C14—C9—C10—C11	-0.2 (5)	C16—C17—C18—C19	-177.8 (4)
O1—C9—C10—C11	-179.9 (3)	S1—C17—C18—C19	0.1 (4)
C9—C10—C11—C12	-0.9 (5)	C17—C18—C19—C20	-0.5 (6)
C10—C11—C12—C13	1.7 (5)	C18—C19—C20—S1	0.6 (5)
C10—C11—C12—C15	177.4 (3)	C17—S1—C20—C19	-0.5 (4)

### Hydrogen-bond geometry ( $\text{\AA}$ , $^\circ$ )

$Cg1$ ,  $Cg2$  and  $Cg3$  are the centroids of the C2–C7, C9–C14 and thiophene rings, respectively.

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1N $\cdots$ O2 <sup>i</sup>	0.87 (4)	2.04 (4)	2.899 (4)	170 (4)
C10—H10 $\cdots$ O1 <sup>ii</sup>	0.95	2.62	3.409 (4)	140
C16—H16 $\cdots$ O2 <sup>i</sup>	0.95	2.49	3.316 (5)	146
C18—H18 $\cdots$ S1 <sup>iii</sup>	0.95	3.00	3.938 (4)	170
C19—H19 $\cdots$ O2 <sup>iv</sup>	0.95	2.65	3.319 (5)	128
C19—H19 $\cdots$ O2 <sup>iv</sup>	0.95	2.65	3.319 (5)	128
C3—H3 $\cdots$ $Cg2^v$	0.95	2.77	3.540 (4)	138
C6—H6 $\cdots$ $Cg1^{vi}$	0.95	2.80	3.593 (4)	141
C14—H14 $\cdots$ $Cg2^i$	0.95	2.90	3.504 (4)	122
C18—H18 $\cdots$ $Cg3^{iii}$	0.95	2.92	3.803 (4)	156

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