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(E)-2-(2,3-Dimethylanilino)-N'-(thiophen-2-ylmethylidene)benzohydrazideHoong-Kun Fun,^{a*} ‡ Tze Shyang Chia,^a Mashooq A. Bhat,^b Mohamed A. Al-Omar^b and Hatem A. Abdel-Aziz^b

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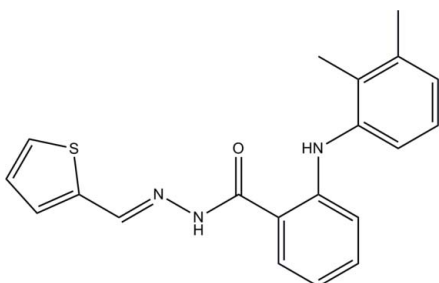
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Key indicators: single-crystal X-ray study; $T = 100$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å; R factor = 0.051; wR factor = 0.128; data-to-parameter ratio = 21.5.

In the title compound, $\text{C}_{20}\text{H}_{19}\text{N}_3\text{OS}$, the central benzene ring makes dihedral angles of 45.36 (9) and 55.33 (9)° with the thiophene ring and the dimethyl-substituted benzene ring, respectively. The dihedral angle between the thiophene ring and dimethyl-substituted benzene ring is 83.60 (9)°. The thiophene ring and the benzene ring are twisted from the mean plane of the $\text{C}(\text{=O})-\text{N}-\text{N}=\text{C}$ bridge [maximum deviation = 0.0860 (13) Å], with dihedral angles of 23.86 (9) and 24.77 (8)°, respectively. An intramolecular $\text{N}-\text{H}\cdots\text{O}$ hydrogen bond generates an $S(6)$ ring. In the crystal, molecules are linked by $\text{N}-\text{H}\cdots\text{O}$ and $\text{C}-\text{H}\cdots\text{O}$ hydrogen bonds to the same acceptor atom, forming sheets lying parallel to the bc plane. The crystal packing also features $\text{C}-\text{H}\cdots\pi$ interactions.

Related literature

For background to the chemistry and biological activity of diaryl amines, see: Reddy *et al.* (2010). For related structures, see: Bhat *et al.* (2012a,b,c); Wang *et al.* (2010); Tian *et al.* (2010). For hydrogen-bond motifs, see: Bernstein *et al.* (1995). For reference bond-length data, see: Allen *et al.* (1987). For the stability of the temperature controller used for the data collection, see: Cosier & Glazer (1986).



‡ Thomson Reuters ResearcherID: A-3561-2009.

Experimental

Crystal data

$\text{C}_{20}\text{H}_{19}\text{N}_3\text{OS}$
 $M_r = 349.44$
 Monoclinic, $P2_1/c$
 $a = 14.0922$ (14) Å
 $b = 15.9682$ (15) Å
 $c = 8.1338$ (8) Å
 $\beta = 105.344$ (2)°
 $V = 1765.1$ (3) Å³
 $Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 0.20$ mm⁻¹
 $T = 100$ K
 $0.34 \times 0.07 \times 0.04$ mm

Data collection

Bruker APEX DUO CCD diffractometer
 Absorption correction: multi-scan (SADABS; Bruker, 2009)
 $T_{\min} = 0.936$, $T_{\max} = 0.992$
 14626 measured reflections
 5082 independent reflections
 3338 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.067$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.051$
 $wR(F^2) = 0.128$
 $S = 1.01$
 5082 reflections
 236 parameters
 H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\text{max}} = 0.37$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.35$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

Cg1 and Cg2 are the centroids of the S1/C15-C18 and C1-C6 rings, respectively.

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{N2}-\text{H1N2}\cdots\text{O1}^{\text{i}}$	0.89 (2)	1.96 (2)	2.808 (2)	160 (2)
$\text{N1}-\text{H1N1}\cdots\text{O1}$	0.85 (2)	2.02 (3)	2.704 (2)	137 (2)
$\text{C1}-\text{H1A}\cdots\text{O1}^{\text{ii}}$	0.95	2.58	3.410 (2)	146
$\text{C3}-\text{H3A}\cdots\text{Cg1}^{\text{iii}}$	0.95	2.98	3.732 (2)	137
$\text{C9}-\text{H9A}\cdots\text{Cg2}^{\text{iv}}$	0.95	2.84	3.649 (2)	144

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

Data collection: APEX2 (Bruker, 2009); cell refinement: SAINT (Bruker, 2009); data reduction: SAINT; program(s) used to solve structure: SHELXTL (Sheldrick, 2008); program(s) used to refine structure: SHELXTL; molecular graphics: SHELXTL; software used to prepare material for publication: SHELXTL and PLATON (Spek, 2009).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB6898).

References

- Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. S1–19.
 Bernstein, J., Davis, R. E., Shimon, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
 Bhat, M. A., Abdel-Aziz, H. A., Ghabbour, H. A., Hemamalini, M. & Fun, H.-K. (2012a). *Acta Cryst.* **E68**, o1002.

- Bhat, M. A., Abdel-Aziz, H. A., Ghabbour, H. A., Hemamalini, M. & Fun, H.-K. (2012b). *Acta Cryst.* **E68**, o1135.
- Bhat, M. A., Abdel-Aziz, H. A., Ghabbour, H. A., Hemamalini, M. & Fun, H.-K. (2012c). *Acta Cryst.* **E68**, o1144–o1145.
- Bruker (2009). *SADABS*, *APEX2* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Cosier, J. & Glazer, A. M. (1986). *J. Appl. Cryst.* **19**, 105–107.
- Reddy, L. V., Suman, A., Beevi, S. S., Mangamoori, L. N., Mukkanti, K. & Pal, S. (2010). *J. Braz. Chem. Soc.* **21**, 98–104.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Spek, A. L. (2009). *Acta Cryst.* **D65**, 148–155.
- Tian, X., Xie, Y.-S. & Zuo, H. (2010). *Acta Cryst.* **E66**, o2828.
- Wang, L.-Y., Xie, Y.-S., Wu, R.-M. & Zuo, H. (2010). *Acta Cryst.* **E66**, o2827.

supporting information

Acta Cryst. (2012). E68, o2524–o2525 [https://doi.org/10.1107/S160053681203259X]

(E)-2-(2,3-Dimethylanilino)-N'-(thiophen-2-ylmethylidene)benzohydrazide

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S1. Comment

In view of the importance of the chemistry and biological activity of diaryl amines (Reddy *et al.*, 2010) and in continuation to our interest in the chemistry of hydrazones (Bhat *et al.*, 2012*a,b,c*), we report herein the crystal structure of the title compound.

The asymmetric unit of the title compound is shown in Fig. 1. The central benzene ring [C7–C12] makes dihedral angles of 45.36 (9)° and 55.33 (9)° with the thiophene ring [S1/C15–C18] and dimethyl-substituted benzene ring [C1–C6], respectively. The dihedral angle between the thiophene ring and C1–C6 benzene ring is 83.60 (9)°. The thiophene ring and C7–C12 benzene ring are twisted from the mean plane of C13(=O1)—N2—N3=C14 bridge [maximum deviation = 0.0860 (13) Å at atom N3] with dihedral angles of 23.86 (9)° and 24.77 (8)°, respectively. An intramolecular N1—H1N1···O1 hydrogen bond generates an S(6) ring motif (Bernstein *et al.*, 1995) in the molecule. Bond lengths (Allen *et al.*, 1987) and angles are within normal ranges and are comparable to those found in related structures (Tian *et al.*, 2010; Wang *et al.*, 2010).

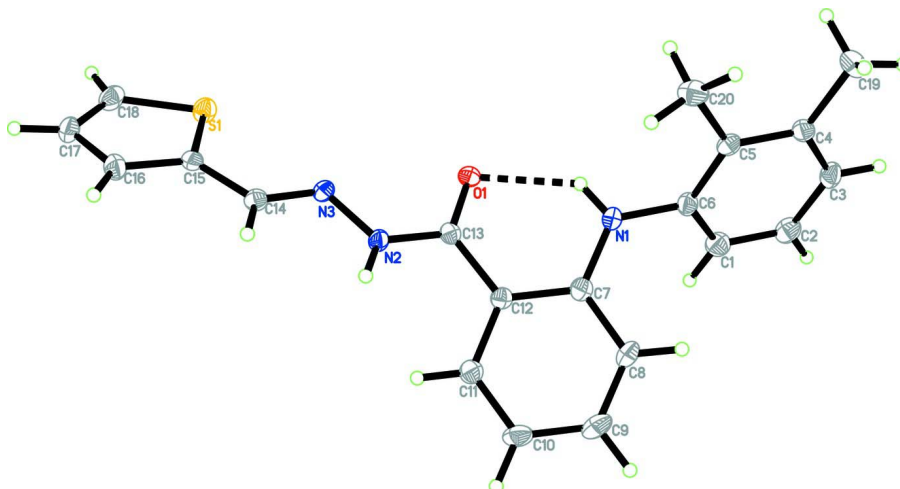
In the crystal (Fig. 2), molecules are linked by N2—H1N2···O1 and C1—H1A···O1 hydrogen bonds, with the same O atom acting as the acceptor, into sheets parallel to *bc* plane. The crystal packing also features C—H··· π interactions (Table 1), involving *Cg*1 and *Cg*2 which are the centroids of S1/C15–C18 and C1–C6 rings, respectively.

S2. Experimental

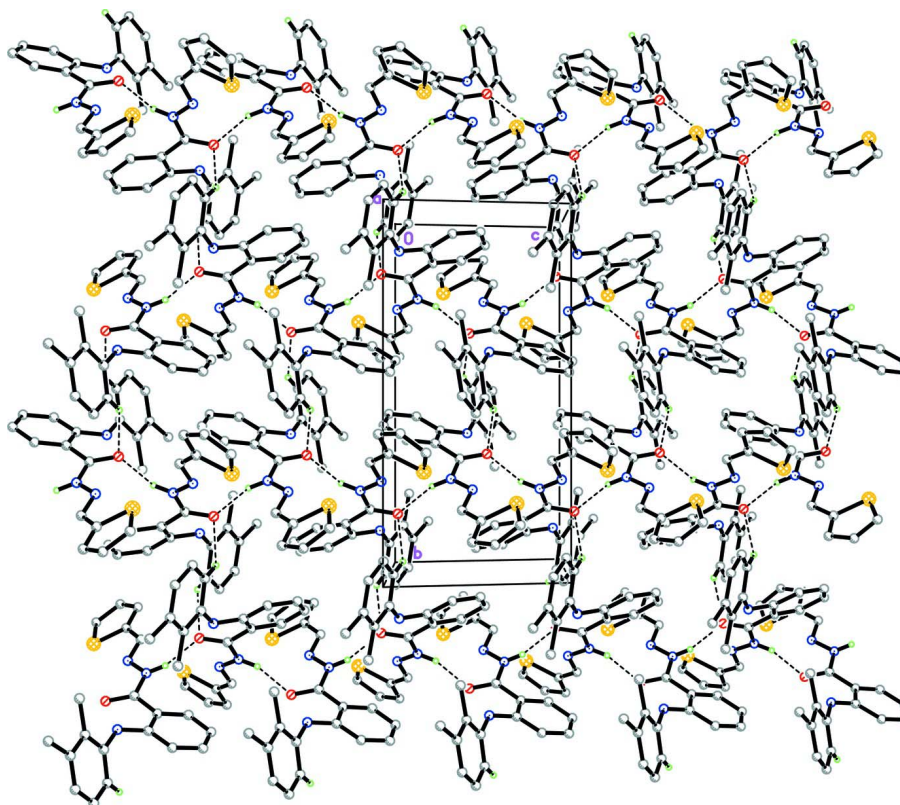
The title compound was prepared by the reaction of thiophene-2-carbaldehyde (0.11 g, 1 mmol) and 2-[(2,3-dimethylphenylamine)]benzohydrazide (0.25 g, 1 mmol) in ethanol (25 ml). After stirring at room temperature for 3 h, the resulting mixture was concentrated under reduced pressure. The precipitate was washed with cold ethanol to afford the title compound. Yellow needles were recrystallized from ethanol solution by the slow evaporation of the solvent at room temperature after several days.

S3. Refinement

The N-bound H atoms were located in a difference Fourier map and refined freely [N—H = 0.85 (3) and 0.89 (2) Å]. The remaining H atoms were positioned geometrically [C—H = 0.95 and 0.98 Å] and refined using a riding model with $U_{\text{iso}}(\text{H}) = 1.2$ or $1.5U_{\text{eq}}(\text{C})$. A rotating group model was applied to the methyl groups. Two outliers, (302) and (312), were omitted in the final refinement.

**Figure 1**

The molecular structure of the title compound with 50% probability displacement ellipsoids. The dashed line represents the intramolecular N—H \cdots O hydrogen bond.

**Figure 2**

The crystal packing of the title compound. The dashed lines represent the hydrogen bonds. For clarity sake, hydrogen atoms not involved in hydrogen bonding have been omitted.

(E)-2-(2,3-Dimethylanilino)-N'-(thiophen-2-ylmethylidene)benzohydrazide*Crystal data*C₂₀H₁₉N₃OS $M_r = 349.44$ Monoclinic, $P2_1/c$

Hall symbol: -P 2ybc

 $a = 14.0922$ (14) Å $b = 15.9682$ (15) Å $c = 8.1338$ (8) Å $\beta = 105.344$ (2)° $V = 1765.1$ (3) Å³ $Z = 4$ $F(000) = 736$ $D_x = 1.315$ Mg m⁻³Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 1664 reflections

 $\theta = 2.9$ – 24.3 ° $\mu = 0.20$ mm⁻¹ $T = 100$ K

Needle, yellow

 $0.34 \times 0.07 \times 0.04$ mm*Data collection*

Bruker APEX DUO CCD

diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

 φ and ω scans

Absorption correction: multi-scan

(SADABS; Bruker, 2009)

 $T_{\min} = 0.936$, $T_{\max} = 0.992$

14626 measured reflections

5082 independent reflections

3338 reflections with $I > 2\sigma(I)$ $R_{\text{int}} = 0.067$ $\theta_{\text{max}} = 30.0$ °, $\theta_{\text{min}} = 1.5$ ° $h = -18 \rightarrow 19$ $k = -18 \rightarrow 22$ $l = -11 \rightarrow 11$ *Refinement*Refinement on F^2

Least-squares matrix: full

 $R[F^2 > 2\sigma(F^2)] = 0.051$ $wR(F^2) = 0.128$ $S = 1.01$

5082 reflections

236 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 atoms treated by a mixture of independent and constrained refinement

 $w = 1/[\sigma^2(F_o^2) + (0.0527P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\text{max}} < 0.001$ $\Delta\rho_{\text{max}} = 0.37$ e Å⁻³ $\Delta\rho_{\text{min}} = -0.35$ e Å⁻³*Special details***Experimental.** The crystal was placed in the cold stream of an Oxford Cryosystems Cobra open-flow nitrogen cryostat (Cosier & Glazer, 1986) operating at 100.0 (1) K.**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 (Å²)*

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
S1	0.10235 (4)	0.29345 (3)	0.79119 (6)	0.02004 (13)
O1	0.44269 (10)	0.16844 (8)	0.95045 (15)	0.0164 (3)

N1	0.63024 (13)	0.11358 (11)	1.0630 (2)	0.0221 (4)
N2	0.38625 (12)	0.23505 (10)	1.1518 (2)	0.0152 (3)
N3	0.30320 (11)	0.26223 (9)	1.03158 (19)	0.0152 (3)
C1	0.72104 (15)	-0.01298 (12)	1.0366 (2)	0.0219 (4)
H1A	0.6781	-0.0443	1.0854	0.026*
C2	0.79626 (16)	-0.05289 (12)	0.9882 (3)	0.0225 (4)
H2A	0.8060	-0.1114	1.0056	0.027*
C3	0.85748 (15)	-0.00697 (12)	0.9138 (2)	0.0209 (4)
H3A	0.9097	-0.0344	0.8817	0.025*
C4	0.84361 (14)	0.07824 (12)	0.8855 (2)	0.0173 (4)
C5	0.76785 (14)	0.12003 (11)	0.9365 (2)	0.0164 (4)
C6	0.70796 (14)	0.07299 (12)	1.0141 (2)	0.0171 (4)
C7	0.60869 (14)	0.10490 (11)	1.2183 (2)	0.0170 (4)
C8	0.67460 (15)	0.06586 (12)	1.3575 (2)	0.0203 (4)
H8A	0.7349	0.0443	1.3442	0.024*
C9	0.65339 (16)	0.05829 (12)	1.5130 (3)	0.0239 (4)
H9A	0.6989	0.0310	1.6044	0.029*
C10	0.56674 (16)	0.08987 (12)	1.5376 (2)	0.0233 (4)
H10A	0.5523	0.0841	1.6447	0.028*
C11	0.50153 (15)	0.13000 (11)	1.4038 (2)	0.0188 (4)
H11A	0.4420	0.1519	1.4203	0.023*
C12	0.52102 (14)	0.13927 (11)	1.2440 (2)	0.0150 (4)
C13	0.44837 (13)	0.18131 (11)	1.1041 (2)	0.0142 (4)
C14	0.25109 (14)	0.31569 (11)	1.0879 (2)	0.0163 (4)
H14A	0.2759	0.3391	1.1983	0.020*
C15	0.15535 (14)	0.34032 (11)	0.9847 (2)	0.0156 (4)
C16	0.09047 (15)	0.39305 (12)	1.0313 (3)	0.0207 (4)
H16A	0.1061	0.4246	1.1340	0.025*
C17	-0.00236 (15)	0.39559 (13)	0.9101 (3)	0.0234 (4)
H17A	-0.0560	0.4289	0.9222	0.028*
C18	-0.00604 (15)	0.34505 (12)	0.7747 (3)	0.0227 (4)
H18A	-0.0625	0.3390	0.6811	0.027*
C19	0.90953 (17)	0.12491 (14)	0.7978 (3)	0.0294 (5)
H19A	0.9586	0.0863	0.7748	0.044*
H19B	0.9430	0.1704	0.8716	0.044*
H19C	0.8698	0.1483	0.6901	0.044*
C20	0.75020 (17)	0.21221 (12)	0.9033 (3)	0.0241 (4)
H20A	0.7177	0.2355	0.9857	0.036*
H20B	0.7081	0.2205	0.7875	0.036*
H20C	0.8133	0.2407	0.9149	0.036*
H1N2	0.3987 (16)	0.2551 (13)	1.257 (3)	0.024 (6)*
H1N1	0.5850 (19)	0.1361 (15)	0.985 (3)	0.035 (7)*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0187 (3)	0.0212 (2)	0.0189 (2)	0.0013 (2)	0.00243 (18)	-0.00158 (19)
O1	0.0181 (7)	0.0193 (6)	0.0122 (6)	0.0016 (5)	0.0045 (5)	-0.0001 (5)

N1	0.0172 (9)	0.0300 (9)	0.0203 (9)	0.0093 (7)	0.0073 (7)	0.0073 (7)
N2	0.0136 (8)	0.0194 (8)	0.0116 (7)	0.0030 (6)	0.0013 (6)	-0.0016 (6)
N3	0.0127 (8)	0.0180 (7)	0.0134 (7)	0.0012 (6)	0.0008 (6)	0.0013 (6)
C1	0.0206 (10)	0.0214 (10)	0.0231 (10)	-0.0019 (8)	0.0047 (8)	0.0026 (8)
C2	0.0260 (11)	0.0164 (9)	0.0239 (10)	0.0038 (8)	0.0046 (9)	0.0002 (8)
C3	0.0191 (10)	0.0230 (10)	0.0201 (10)	0.0064 (8)	0.0044 (8)	-0.0023 (8)
C4	0.0163 (10)	0.0212 (9)	0.0141 (9)	-0.0002 (7)	0.0036 (7)	-0.0004 (7)
C5	0.0172 (10)	0.0169 (9)	0.0128 (9)	0.0003 (7)	-0.0001 (7)	-0.0004 (7)
C6	0.0136 (9)	0.0208 (9)	0.0163 (9)	0.0013 (7)	0.0029 (7)	-0.0004 (7)
C7	0.0164 (9)	0.0165 (9)	0.0174 (9)	0.0001 (7)	0.0036 (7)	-0.0006 (7)
C8	0.0159 (10)	0.0215 (9)	0.0203 (10)	0.0031 (8)	-0.0012 (8)	0.0011 (8)
C9	0.0267 (11)	0.0222 (10)	0.0171 (10)	0.0029 (9)	-0.0042 (8)	0.0003 (8)
C10	0.0319 (12)	0.0239 (10)	0.0126 (9)	0.0030 (9)	0.0030 (8)	0.0005 (8)
C11	0.0201 (10)	0.0188 (9)	0.0174 (9)	0.0025 (8)	0.0050 (8)	-0.0007 (7)
C12	0.0142 (9)	0.0157 (8)	0.0143 (9)	-0.0016 (7)	0.0025 (7)	-0.0005 (7)
C13	0.0127 (9)	0.0142 (8)	0.0160 (9)	-0.0022 (7)	0.0042 (7)	-0.0002 (7)
C14	0.0171 (10)	0.0170 (9)	0.0141 (9)	-0.0004 (7)	0.0029 (7)	-0.0003 (7)
C15	0.0151 (9)	0.0169 (9)	0.0155 (9)	0.0003 (7)	0.0053 (7)	0.0029 (7)
C16	0.0209 (10)	0.0226 (10)	0.0195 (10)	0.0042 (8)	0.0068 (8)	-0.0013 (8)
C17	0.0177 (10)	0.0257 (10)	0.0280 (11)	0.0076 (8)	0.0083 (8)	0.0073 (9)
C18	0.0151 (10)	0.0250 (10)	0.0253 (11)	-0.0001 (8)	0.0009 (8)	0.0060 (8)
C19	0.0262 (12)	0.0360 (12)	0.0306 (12)	0.0019 (10)	0.0156 (10)	0.0064 (9)
C20	0.0335 (12)	0.0182 (9)	0.0225 (10)	0.0016 (9)	0.0107 (9)	0.0003 (8)

Geometric parameters (Å, °)

S1—C18	1.709 (2)	C8—C9	1.380 (3)
S1—C15	1.7243 (19)	C8—H8A	0.9500
O1—C13	1.248 (2)	C9—C10	1.384 (3)
N1—C7	1.382 (2)	C9—H9A	0.9500
N1—C6	1.417 (2)	C10—C11	1.382 (3)
N1—H1N1	0.85 (3)	C10—H10A	0.9500
N2—C13	1.354 (2)	C11—C12	1.406 (3)
N2—N3	1.382 (2)	C11—H11A	0.9500
N2—H1N2	0.89 (2)	C12—C13	1.475 (3)
N3—C14	1.287 (2)	C14—C15	1.442 (3)
C1—C2	1.381 (3)	C14—H14A	0.9500
C1—C6	1.391 (3)	C15—C16	1.368 (3)
C1—H1A	0.9500	C16—C17	1.415 (3)
C2—C3	1.387 (3)	C16—H16A	0.9500
C2—H2A	0.9500	C17—C18	1.355 (3)
C3—C4	1.385 (3)	C17—H17A	0.9500
C3—H3A	0.9500	C18—H18A	0.9500
C4—C5	1.411 (3)	C19—H19A	0.9800
C4—C19	1.510 (3)	C19—H19B	0.9800
C5—C6	1.399 (3)	C19—H19C	0.9800
C5—C20	1.505 (3)	C20—H20A	0.9800
C7—C8	1.406 (3)	C20—H20B	0.9800

C7—C12	1.417 (3)	C20—H20C	0.9800
C18—S1—C15	91.42 (10)	C9—C10—H10A	120.5
C7—N1—C6	125.71 (17)	C10—C11—C12	121.68 (18)
C7—N1—H1N1	115.0 (17)	C10—C11—H11A	119.2
C6—N1—H1N1	117.7 (16)	C12—C11—H11A	119.2
C13—N2—N3	119.15 (15)	C11—C12—C7	119.14 (17)
C13—N2—H1N2	121.9 (15)	C11—C12—C13	119.70 (17)
N3—N2—H1N2	118.9 (15)	C7—C12—C13	121.12 (16)
C14—N3—N2	114.37 (15)	O1—C13—N2	121.08 (17)
C2—C1—C6	120.20 (18)	O1—C13—C12	123.01 (16)
C2—C1—H1A	119.9	N2—C13—C12	115.90 (15)
C6—C1—H1A	119.9	N3—C14—C15	120.51 (17)
C1—C2—C3	119.58 (18)	N3—C14—H14A	119.7
C1—C2—H2A	120.2	C15—C14—H14A	119.7
C3—C2—H2A	120.2	C16—C15—C14	126.67 (17)
C4—C3—C2	120.99 (19)	C16—C15—S1	111.12 (15)
C4—C3—H3A	119.5	C14—C15—S1	121.70 (14)
C2—C3—H3A	119.5	C15—C16—C17	112.75 (18)
C3—C4—C5	120.02 (17)	C15—C16—H16A	123.6
C3—C4—C19	119.07 (18)	C17—C16—H16A	123.6
C5—C4—C19	120.90 (17)	C18—C17—C16	112.26 (18)
C6—C5—C4	118.19 (17)	C18—C17—H17A	123.9
C6—C5—C20	121.03 (17)	C16—C17—H17A	123.9
C4—C5—C20	120.76 (17)	C17—C18—S1	112.46 (16)
C1—C6—C5	120.97 (18)	C17—C18—H18A	123.8
C1—C6—N1	119.99 (17)	S1—C18—H18A	123.8
C5—C6—N1	118.97 (17)	C4—C19—H19A	109.5
N1—C7—C8	121.51 (18)	C4—C19—H19B	109.5
N1—C7—C12	120.46 (17)	H19A—C19—H19B	109.5
C8—C7—C12	117.96 (17)	C4—C19—H19C	109.5
C9—C8—C7	121.33 (19)	H19A—C19—H19C	109.5
C9—C8—H8A	119.3	H19B—C19—H19C	109.5
C7—C8—H8A	119.3	C5—C20—H20A	109.5
C8—C9—C10	120.95 (18)	C5—C20—H20B	109.5
C8—C9—H9A	119.5	H20A—C20—H20B	109.5
C10—C9—H9A	119.5	C5—C20—H20C	109.5
C11—C10—C9	118.90 (18)	H20A—C20—H20C	109.5
C11—C10—H10A	120.5	H20B—C20—H20C	109.5
C13—N2—N3—C14	-177.33 (16)	C9—C10—C11—C12	0.1 (3)
C6—C1—C2—C3	-1.3 (3)	C10—C11—C12—C7	1.5 (3)
C1—C2—C3—C4	-0.7 (3)	C10—C11—C12—C13	178.95 (17)
C2—C3—C4—C5	1.6 (3)	N1—C7—C12—C11	-179.49 (18)
C2—C3—C4—C19	-177.56 (18)	C8—C7—C12—C11	-2.7 (3)
C3—C4—C5—C6	-0.4 (3)	N1—C7—C12—C13	3.1 (3)
C19—C4—C5—C6	178.70 (18)	C8—C7—C12—C13	179.91 (17)
C3—C4—C5—C20	-178.59 (18)	N3—N2—C13—O1	13.8 (3)

C19—C4—C5—C20	0.6 (3)	N3—N2—C13—C12	-165.63 (15)
C2—C1—C6—C5	2.5 (3)	C11—C12—C13—O1	-155.40 (18)
C2—C1—C6—N1	179.59 (18)	C7—C12—C13—O1	22.0 (3)
C4—C5—C6—C1	-1.6 (3)	C11—C12—C13—N2	24.0 (2)
C20—C5—C6—C1	176.56 (18)	C7—C12—C13—N2	-158.62 (17)
C4—C5—C6—N1	-178.73 (17)	N2—N3—C14—C15	-170.89 (16)
C20—C5—C6—N1	-0.6 (3)	N3—C14—C15—C16	176.61 (19)
C7—N1—C6—C1	49.4 (3)	N3—C14—C15—S1	5.5 (3)
C7—N1—C6—C5	-133.4 (2)	C18—S1—C15—C16	0.06 (15)
C6—N1—C7—C8	12.2 (3)	C18—S1—C15—C14	172.39 (16)
C6—N1—C7—C12	-171.05 (18)	C14—C15—C16—C17	-171.90 (18)
N1—C7—C8—C9	179.14 (19)	S1—C15—C16—C17	0.0 (2)
C12—C7—C8—C9	2.4 (3)	C15—C16—C17—C18	0.0 (3)
C7—C8—C9—C10	-0.8 (3)	C16—C17—C18—S1	0.1 (2)
C8—C9—C10—C11	-0.5 (3)	C15—S1—C18—C17	-0.07 (16)

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

Cg1 and Cg2 are the centroids of the S1/C15–C18 and C1–C6 rings, respectively.

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N2—H1N2 \cdots O1 ⁱ	0.89 (2)	1.96 (2)	2.808 (2)	160 (2)
N1—H1N1 \cdots O1	0.85 (2)	2.02 (3)	2.704 (2)	137 (2)
C1—H1A \cdots O1 ⁱⁱ	0.95	2.58	3.410 (2)	146
C3—H3A \cdots Cg1 ⁱⁱⁱ	0.95	2.98	3.732 (2)	137
C9—H9A \cdots Cg2 ^{iv}	0.95	2.84	3.649 (2)	144

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