

Different conformations and packing motifs in the crystal structures of four thiophene–carbohydrazide–pyridine derivatives

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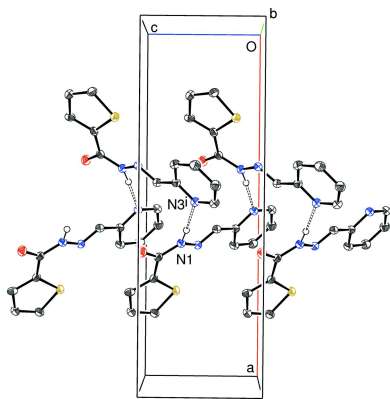
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The crystal structures of four thiophene–carbohydrazide–pyridine derivatives, viz. *N'*-[(*E*)-pyridin-3-ylmethylidene]thiophene-2-carbohydrazide, C₁₁H₉N₃OS, (I), *N'*-[(*E*)-pyridin-2-ylmethylidene]thiophene-2-carbohydrazide, C₁₁H₉N₃OS, (II), *N*-methyl-*N'*-[(*E*)-pyridin-2-ylmethylidene]thiophene-2-carbohydrazide, C₁₂H₁₁N₃OS, (III) and *N'*-[(*E*)-pyridin-2-ylmethylidene]-2-(thiophen-2-yl)ethanohydrazide, C₁₂H₁₁N₃OS, (IV) are described. The dihedral angles between the thiophene ring and the pyridine ring are 21.4 (2), 15.42 (14), 4.97 (8) and 83.52 (13)° for (I)–(IV), respectively. The thiophene ring in (IV) is disordered over two orientations in a 0.851 (2):0.149 (2) ratio. Key features of the packing include N–H···N_p (p = pyridine) hydrogen bonds in (I), which generate *C*(7) chains propagating in the [001] direction; N–H···N_p links also feature in (II), but in this case they lead to *C*(6) [001] chains; in (IV), classical amide (*C*4) N–H···O links result in [010] chains; in every case adjacent molecules in the chains are related by 2₁ screw axes. There are no classical hydrogen bonds in the extended structure of (III). Various weak C–H···*X* (*X* = O, N, S) interactions occur in each structure, but no aromatic π–π stacking is evident. The Hirshfeld surfaces and fingerprint plots for (I)–(IV) are compared.

1. Chemical context

Various thiophene–carbohydrazide derivatives containing a T–C(=O)–NH–N=CH–R (T = thiophene ring) building unit have been previously investigated by some of us for their anti-cancer (Cardoso *et al.*, 2017) and anti-tuberculosis (Cardoso *et al.*, 2014, 2016*a*) properties. Other workers have reported their analgesic activities (Lima *et al.*, 2000) and their potential uses as tunable photo switches (van Dijken *et al.*, 2015). The use of these compounds as multi-dentate chelating ligands has been described by Gholivand *et al.* (2016) and Abbas *et al.* (2021).

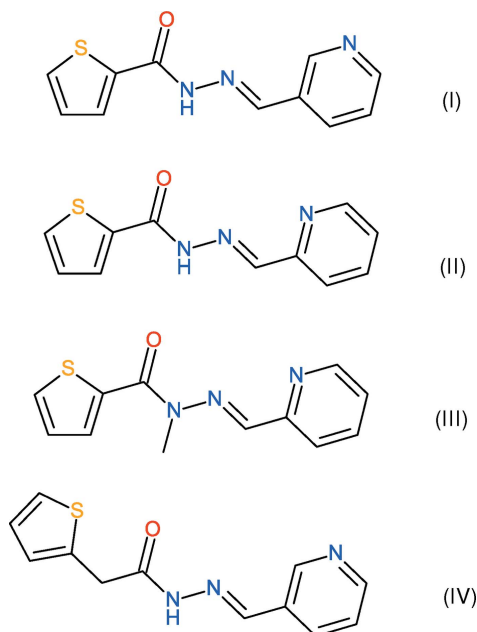
In a continuation of our earlier work on this family of compounds (Cardoso *et al.*, 2016*b,c*), we now describe the crystal structures and Hirshfeld surfaces of *N'*-[(*E*)-pyridin-3-ylmethylidene]thiophene-2-carbohydrazide, C₁₁H₉N₃OS (I), *N'*-[(*E*)-pyridin-2-ylmethylidene]thiophene-2-carbohydrazide, C₁₁H₉N₃OS (II), *N*-methyl-*N'*-[(*E*)-pyridin-2-ylmethylidene]thiophene-2-carbohydrazide, C₁₂H₁₁N₃OS (III) and *N'*-[(*E*)-pyridin-2-ylmethylidene]-2-(thiophen-2-yl)ethanohydrazide, C₁₂H₁₁N₃OS (IV). Compounds (I) and (II) are positional isomers, differing in the location of the N atom of the pyridine ring, (III) is a methylated derivative of (II) and (IV) has a



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methylene group inserted between the thiophene ring and the carbohydrazide grouping compared to (I).



2. Structural commentary

The molecular structures of (I)–(IV) are shown in Figs. 1–4, respectively and they all confirm the structures (atomic connectivities) postulated in the previous studies noted in the synthesis section: each compound crystallizes with one molecule in the asymmetric unit and there is no suggestion that any of these compounds exist in the ‘enol’ –C(OH)=N– tautomer in the solid state.

In (I) (Fig. 1), the conformation about the N2=C6 bond [1.280 (5) Å] is *E* and the C5–N1–N2–C6 torsion angle is 175.1 (4)°. The oxygen atom of the carbonyl group and the sulfur atom of the thiophene ring lie on the same side of the molecule [S1–C4–C5–O1 = –4.9 (6)°] whereas atom N3 of the pyridine ring lies on the opposite side. The dihedral angle between the thiophene and pyridine rings is 21.4 (2)° and the largest twist in the molecule occurs about the C6–C7 bond [N2–C6–C7–C8 = –11.8 (7)°]. The N1–N2 bond length of 1.384 (5) Å in (I) is significantly shorter than a typical N–N single bond (~1.44 Å), which suggests substantial delocalization of electrons with the adjacent C5=O1 carbonyl group

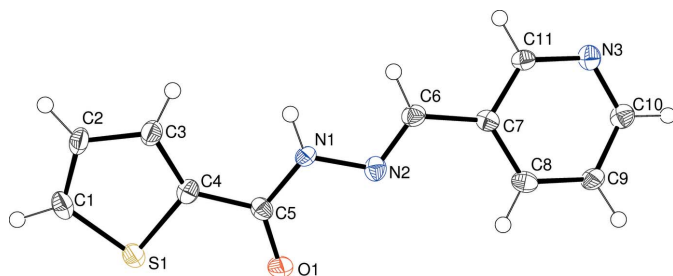


Figure 1
The molecular structure of (I) showing 50% displacement ellipsoids.

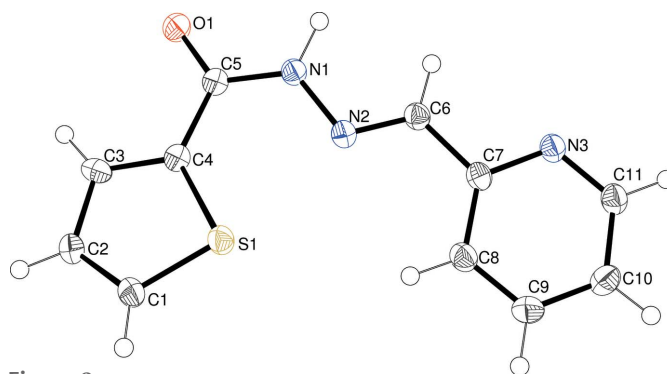


Figure 2
The molecular structure of (II) showing 50% displacement ellipsoids.

and the N2=C6 double bond, as observed previously for related compounds (Cardoso *et al.*, 2016c). Otherwise, the bond lengths and angles in (I) may be regarded as unexceptional.

In (II) (Fig. 2), the N2=C6 double bond [1.284 (3) Å] is also in an *E* configuration and C5–N1–N2–C6 = 173.74 (19)° but unlike (I), atoms O1 and S1 lie on opposite sides of the molecule [S1–C4–C5–O1 = –170.67 (17)°] and N3 lies on the same side as O1. The dihedral angle between the aromatic rings is 15.42 (14)° and the most significant twist occurs about the C5–N1 bond [C4–C5–N1–N2 = 12.0 (3)°]. The C8–H8 bond of the pyridine ring points towards S1 but with H···S = 3.22 Å (sum of van der Waals radii = 3.00 Å) we consider it to be too long to be regarded as an intramolecular hydrogen bond.

Compound (III) (Fig. 3) is the *N*-methylated derivative of (II): the N2=C7 bond [1.2815 (17) Å] has an *E* configuration and C5–N1–N2–C7 = 179.40 (12)°. As with (II), O1 and S1 lie on opposite sides of the molecule [S1–C4–C5–O1 = 178.88 (10)°] and N3 lies on the same side as O1. The dihedral angle between the C1–C4/S1 and C8–C12/N3 rings is 4.97 (8)°: most of this twist appear to be about the C7–C8 bond [N2–C7–C8–C9 = –4.8 (2)°] although the whole molecule is close to flat [r.m.s. deviation for the 17 non-H atoms = 0.065 Å]. In this case, the short intramolecular H···S contact

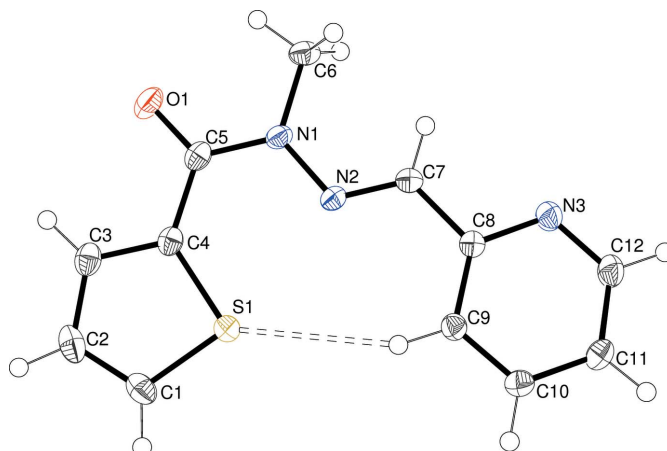


Figure 3
The molecular structure of (III) showing 50% displacement ellipsoids. The short C–H···S contact is indicated by a double-dashed line.

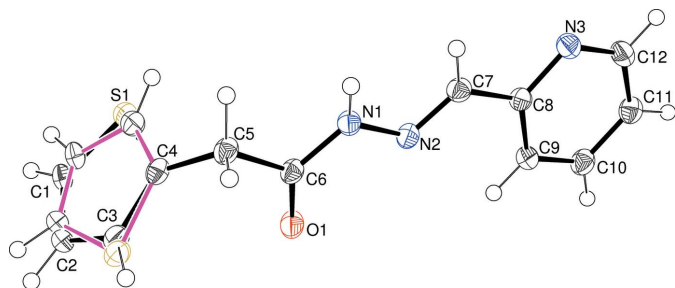


Figure 4
The molecular structure of (IV) showing 50% displacement ellipsoids. The minor disorder component of the thiophene ring is shown with pink bonds.

between C9–H9 and S1 is 2.84 Å ($C-H \cdots S = 155^\circ$), considerably shorter than the equivalent contact in (II), and reasonable for this type of weak interaction (Ghosh *et al.*, 2020).

In (IV) (Fig. 4), the thiophene ring was modelled with ‘flip’ disorder ($\sim 180^\circ$ rotation about the C4–C5 bond) in a 0.851 (2):0.149 (2) ratio, which is a common structural feature for this moiety (Cardoso *et al.*, 2016c). Once again, the configuration of the $N2=C7$ double bond [1.281 (2) Å] is *E* and C6 and C7 are close to *anti* about the N–N bond [$C6-N1-N2-C7 = -177.90 (14)^\circ$]. The dihedral angle between the aromatic rings (major disorder conformation for the thiophene moiety) in (IV) of $83.52 (13)^\circ$ indicates near perpendicularity, which is quite different to the other compounds described here, presumably because the molecule has additional conformational flexibility about the C–C single bonds associated with the C5 methylene group [$C3-C4-C5-C6 = 93.8 (6)^\circ$; $C4-C5-C6-N1 = 144.72 (14)^\circ$].

3. Supramolecular features

Geometrical data for the directional intermolecular interactions in (I)–(IV) are listed in Tables 1–4, respectively. The most significant features in the packing of (I) and (II) are N–

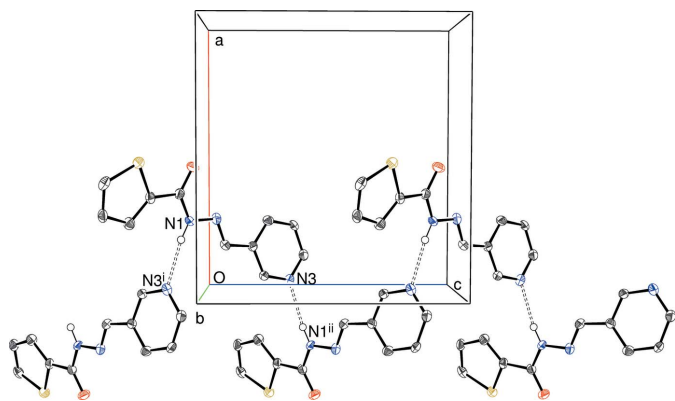


Figure 5
Fragment of the crystal structure of (I) showing part of an [001] $C(7)$ chain linked by N–H \cdots N hydrogen bonds (double dashed lines). Symmetry codes: (i) $-x, -y, z - \frac{1}{2}$; (ii) $-x, -y, z + \frac{1}{2}$.

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

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$N1-H1N \cdots N3^i$	0.87 (5)	2.14 (5)	2.995 (5)	166 (4)
$C1-H1 \cdots O1^{ii}$	0.95	2.53	3.471 (6)	171
$C3-H3 \cdots N3^i$	0.95	2.61	3.479 (6)	152
$C6-H6 \cdots N3^i$	0.95	2.59	3.410 (6)	145
$C9-H9 \cdots O1^{iii}$	0.95	2.66	3.397 (5)	135
$C11-H11 \cdots N2^{iv}$	0.95	2.57	3.481 (6)	160

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

Table 2
Hydrogen-bond geometry (Å, °) for (II).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$N1-H1N \cdots N3^i$	0.98 (3)	2.03 (3)	3.013 (3)	177 (3)
$C1-H1 \cdots O1^{ii}$	0.95	2.48	3.101 (3)	123
$C2-H2 \cdots O1^{iii}$	0.95	2.64	3.410 (3)	139

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

Table 3
Hydrogen-bond geometry (Å, °) for (III).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$C9-H9 \cdots S1$	0.95	2.84	3.7217 (13)	155
$C6-H6C \cdots N3^i$	0.98	2.61	3.3499 (18)	132

Symmetry code: (i) $-x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$.

Table 4
Hydrogen-bond geometry (Å, °) for (IV).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$N1-H1N \cdots O1^i$	0.88 (2)	2.00 (2)	2.8628 (18)	164.9 (18)
$C3-H3 \cdots N1^{ii}$	0.95	2.78	3.718 (7)	172
$C5-H5B \cdots O1^i$	0.99	2.64	3.307 (2)	125
$C7-H7 \cdots S1B^i$	0.95	2.65	3.534 (16)	155
$C12-H12 \cdots S1^{iii}$	0.95	2.98	3.6624 (19)	129

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

$H \cdots N_p$ ($p = \text{pyridine}$) hydrogen bonds: in the former, these links generate [001] $C(7)$ chains (Fig. 5), with adjacent molecules in the chain related by the 2_1 screw axis. In (II), the equivalent interaction also leads to [001] chains (Fig. 6) generated by the 2_1 screw axis but here the graph-set motif is $C(6)$. The packing for (IV) features classical $C(4)$ amide N–H \cdots O hydrogen bonds (Fig. 7) leading to [010] chains generated once again by a 2_1 screw axis. There are obviously no classical hydrogen bonds in the extended structure of (III) and the only possible directional intermolecular contact identified is a very weak $C-H \cdots N_p$ link arising from the *N*-methyl group. The structures of (I), (II) and (IV) also feature various $C-H \cdots X$ ($X = N, O, S$) interactions although these are presumably very weak, given their $H \cdots X$ lengths.

The shortest aromatic ring centroid–centroid separations in these structures are $\pi_t \cdots \pi_p$ ($t = \text{thiophene}$, $p = \text{pyridine}$) = 4.046 (2) Å (slippage = 1.546 Å) for (I), $\pi_t \cdots \pi_p$ = 4.0509 (12) Å (slippage = 1.929 Å) for (II), $\pi_t \cdots \pi_p$ = 4.7831 (9) Å for (III) and $\pi_t \cdots \pi_p$ = 4.643 (2) Å for (IV).

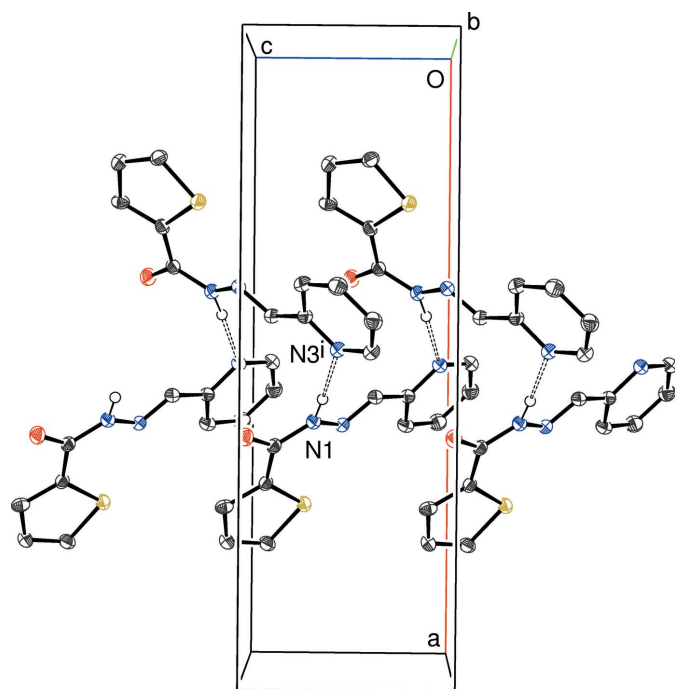


Figure 6
Fragment of the crystal structure of (II) showing part of an [001] $C(6)$ chain linked by $N-H\cdots N$ hydrogen bonds (double-dashed lines). Symmetry code: (i) $1 - x, 1 - y, z + \frac{1}{2}$.

Given these distances, any aromatic ring-stacking effects that contribute to the cohesion and stability of the crystal must be weak to non-existent.

In order to gain more insight into these different packing motifs, the Hirshfeld surfaces and fingerprint plots for (I)–(IV) were calculated using *CrystalExplorer* (Turner *et al.*, 2017) following the approach recently described by Tan *et al.* (2019). The Hirshfeld surfaces (see supporting information) show the expected red spots (close contacts) in the vicinities of the various donor and acceptor atoms.

The fingerprint plots for (I)–(IV) decomposed into the different percentage contact types (Table 5) show that the different contributions are broadly similar, with $H\cdots H$ (van der Waals) contacts the most significant for each structure, followed by $C\cdots H/H\cdots C$. The $O\cdots H/H\cdots O$ and $N\cdots H/H\cdots N$ contributions are almost the same for the four structures, despite the lack of classical hydrogen bonds in (III). The $S\cdots H/H\cdots S$ percentage contributions for (I) and (IV) are notably greater than those for (II) and (III), possibly because the S atom is ‘facing outwards’ in the former structures but is associated with an intramolecular $C-H\cdots S$ close contact arising from the pyridine ring in the latter structures. It is notable that the percentage of $O\cdots O$ contacts is zero in all structures, presumably reflecting the fact that ‘bare’ O atoms avoid each other in the solid state for electrostatic reasons.

4. Database survey

A survey of the Cambridge Structural Database (CSD Core 2012.3 version of March 2022; Groom *et al.*, 2016) revealed

Table 5
Hirshfeld fingerprint contact percentages for (I)–(IV).

Contact type	(I)	(II)	(III)	(IV) ^a
$H\cdots H$	30.1	32.8	36.5	34.5
$C\cdots H/H\cdots C$	15.1	23.3	28.2	22.6
$O\cdots H/H\cdots O$	13.1	12.8	10.4	11.2
$N\cdots H/H\cdots N$	13.7	12.2	11.5	13.8
$S\cdots H/H\cdots S$	12.1	7.0	5.8	10.7
$C\cdots C$	6.2	4.5	1.8	1.2
$C\cdots O/O\cdots C$	1.3	0.8	0.7	1.0
$O\cdots O$	0.0	0.0	0.0	0.0

Note: (a) Major disorder component.

nine structures incorporating the $T-C(=O)-NH-N=CH-Q$ (T = thiophene ring; Q = thiophene or furan or pyrrole ring or derivatives) grouping and two with the $T-CH_2-C(=O)-NH-N=CH-Q$ sequence. None of these structures features a pyridine ring in the ‘Q’ position.

5. Synthesis and crystallization

Compounds (I) and (II) were prepared by a literature procedure (Lima *et al.*, 2000) and single crystals suitable for data collection were recrystallized from ethanol solution at room temperature. For the syntheses and spectroscopic characterizations of (III) and (IV), see Cardoso *et al.* (2016a) and

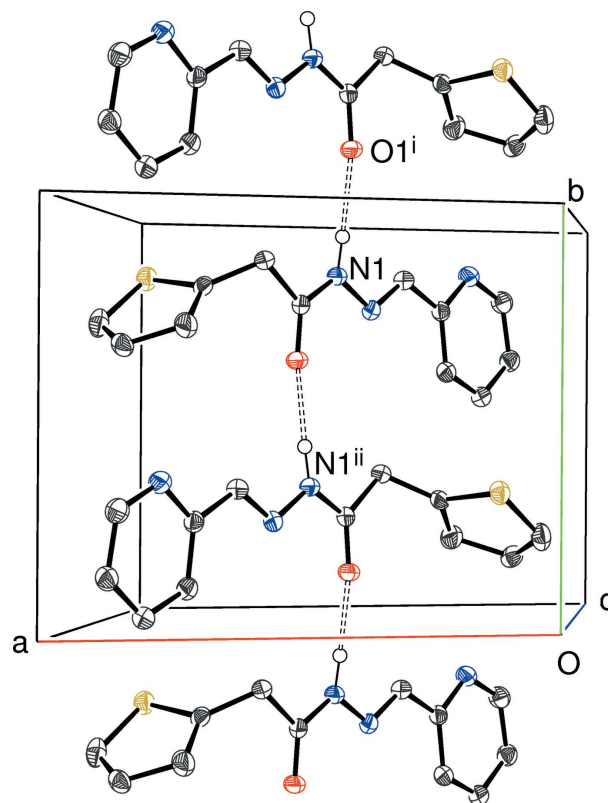


Figure 7
Fragment of the crystal structure of (IV) showing part of an [010] $C(4)$ chain linked by $N-H\cdots O$ hydrogen bonds (double-dashed lines). Symmetry codes: (i) $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$; (ii) $1 - x, y - \frac{1}{2}, \frac{1}{2} - z$.

Table 6
Experimental details.

	(I)	(II)	(III)	(IV)
Crystal data				
Chemical formula	C ₁₁ H ₉ N ₃ OS	C ₁₁ H ₉ N ₃ OS	C ₁₂ H ₁₁ N ₃ OS	C ₁₂ H ₁₁ N ₃ OS
<i>M_r</i>	231.27	231.27	245.30	245.30
Crystal system, space group	Orthorhombic, <i>Pca</i> 2 ₁	Orthorhombic, <i>Pna</i> 2 ₁	Monoclinic, <i>C2/c</i>	Monoclinic, <i>P2₁/c</i>
Temperature (K)	100	100	100	100
<i>a</i> , <i>b</i> , <i>c</i> (Å)	10.6845 (9), 9.4974 (9), 10.0917 (10)	18.4056 (13), 9.5255 (7), 6.0300 (4)	21.0690 (15), 5.1085 (4), 21.1531 (15)	11.3963 (8), 9.2782 (7), 11.8178 (8)
α , β , γ (°)	90, 90, 90	90, 90, 90	90, 95.265 (2), 90	90, 112.761 (2), 90
<i>V</i> (Å ³)	1024.05 (16)	1057.19 (13)	2267.1 (3)	1152.27 (14)
<i>Z</i>	4	4	8	4
Radiation type	Mo <i>K</i> α	Mo <i>K</i> α	Mo <i>K</i> α	Mo <i>K</i> α
μ (mm ⁻¹)	0.30	0.29	0.27	0.27
Crystal size (mm)	0.05 × 0.04 × 0.01	0.15 × 0.06 × 0.04	0.42 × 0.12 × 0.03	0.10 × 0.09 × 0.06
Data collection				
Diffractometer	Rigaku Saturn724+ CCD	Rigaku Saturn724+ CCD	Rigaku Saturn724+ CCD	Rigaku AFC12 CCD
Absorption correction	Multi-scan (<i>CrystalClear</i> ; Rigaku, 2012)	Multi-scan (<i>CrystalClear</i> ; Rigaku, 2012)	Multi-scan (<i>CrystalClear</i> ; Rigaku, 2012)	Multi-scan (<i>CrystalClear</i> ; Rigaku, 2012)
<i>T_{min}</i> , <i>T_{max}</i>	0.484, 1.000	0.756, 1.000	0.780, 1.000	0.723, 1.000
No. of measured, independent and observed [<i>I</i> > 2 σ (<i>I</i>)] reflections	6740, 1822, 1559	7314, 1979, 1930	8717, 2563, 2307	8155, 2593, 2138
<i>R_{int}</i> (<i>sin</i> θ / λ) _{max} (Å ⁻¹)	0.058 0.649	0.026 0.649	0.022 0.650	0.031 0.670
Refinement				
<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.046, 0.112, 1.08	0.029, 0.083, 1.08	0.031, 0.087, 1.07	0.041, 0.112, 1.10
No. of reflections	1822	1979	2563	2593
No. of parameters	148	148	155	170
No. of restraints	1	1	0	10
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	H-atom parameters constrained	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å ⁻³)	0.27, -0.43	0.33, -0.24	0.33, -0.29	0.32, -0.30
Absolute structure	Parsons <i>et al.</i> (2013)	Parsons <i>et al.</i> (2013)	–	–
Absolute structure parameter	0.02 (13)	0.04 (4)	–	–

Computer programs: *CrystalClear* (Rigaku, 2012), *SHELXS97* (Sheldrick, 2008), *SHELXL2018/3* (Sheldrick, 2015), *ORTEP-3 for Windows* (Farrugia, 2012) and *pubCIF* (Westrip, 2010).

Cardoso *et al.* (2014), respectively: in each case, colourless blocks suitable for X-ray data collections were recrystallized from ethanol solution at room temperature.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 6. The thiophene ring in (IV) was modelled as disordered over two sets of sites related by an approximate rotation of 180° about the C4–C5 bond in a 0.851 (2): 0.149 (2) ratio. EADP cards in *SHELXL* were used for the *U_{ij}* values of equivalent atom pairs (*e.g.*, C1 and C1B) and a SAME card was used to restrain the nearest-neighbour and next-nearest-neighbour bond distances in the two disorder components to be equal with standard deviations of 0.02 and 0.04 Å, respectively. The N-bound H atoms in (I), (II) and (IV) were located in difference maps and their positions were freely refined with *U_{iso}*(H) = 1.2*U_{eq}*(N). All C-bound H atoms were located geometrically (C–H = 0.95–0.99 Å) and refined as riding atoms with *U_{iso}*(H) = 1.2*U_{eq}*(C) or 1.5*U_{eq}*(methyl C). The methyl group in (III) was allowed to rotate, but not to tip, to best fit the electron density.

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supporting information

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Different conformations and packing motifs in the crystal structures of four thiophene–carbohydrazide–pyridine derivatives

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Computing details

For all structures, data collection: *CrystalClear* (Rigaku, 2012); cell refinement: *CrystalClear* (Rigaku, 2012); data reduction: *CrystalClear* (Rigaku, 2012); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2018/3* (Sheldrick, 2015); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012); software used to prepare material for publication: *publCIF* (Westrip, 2010).

N'-[(*E*)-Pyridin-3-ylmethylidene]thiophene-2-carbohydrazide (I)

Crystal data

$C_{11}H_9N_3OS$	$D_x = 1.500 \text{ Mg m}^{-3}$
$M_r = 231.27$	Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$
Orthorhombic, $Pca2_1$	Cell parameters from 5861 reflections
$a = 10.6845 (9) \text{ \AA}$	$\theta = 3.5\text{--}27.5^\circ$
$b = 9.4974 (9) \text{ \AA}$	$\mu = 0.30 \text{ mm}^{-1}$
$c = 10.0917 (10) \text{ \AA}$	$T = 100 \text{ K}$
$V = 1024.05 (16) \text{ \AA}^3$	Chip, colourless
$Z = 4$	$0.05 \times 0.04 \times 0.01 \text{ mm}$
$F(000) = 480$	

Data collection

Rigaku Saturn724+ CCD diffractometer	1822 independent reflections
ω scans	1559 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (CrystalClear; Rigaku, 2012)	$R_{\text{int}} = 0.058$
$T_{\text{min}} = 0.484$, $T_{\text{max}} = 1.000$	$\theta_{\text{max}} = 27.5^\circ$, $\theta_{\text{min}} = 3.5^\circ$
6740 measured reflections	$h = -12 \rightarrow 13$
	$k = -12 \rightarrow 12$
	$l = -7 \rightarrow 13$

Refinement

Refinement on F^2	Hydrogen site location: mixed
Least-squares matrix: full	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)] = 0.046$	$w = 1/[\sigma^2(F_o^2) + (0.0492P)^2 + 0.5837P]$
$wR(F^2) = 0.112$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.08$	$(\Delta/\sigma)_{\text{max}} < 0.001$
1822 reflections	$\Delta\rho_{\text{max}} = 0.27 \text{ e \AA}^{-3}$
148 parameters	$\Delta\rho_{\text{min}} = -0.43 \text{ e \AA}^{-3}$
1 restraint	Absolute structure: Parsons <i>et al.</i> (2013)
Primary atom site location: structure-invariant direct methods	Absolute structure parameter: 0.02 (13)

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>	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.4074 (4)	0.5100 (5)	-0.3833 (5)	0.0253 (10)
H1	0.444915	0.579791	-0.437808	0.030*
C2	0.2866 (4)	0.4653 (4)	-0.3959 (5)	0.0239 (10)
H2	0.230294	0.500393	-0.460776	0.029*
C3	0.2544 (4)	0.3608 (4)	-0.3018 (5)	0.0236 (10)
H3	0.173924	0.318696	-0.296656	0.028*
C4	0.3510 (4)	0.3271 (4)	-0.2195 (4)	0.0199 (10)
C5	0.3644 (4)	0.2257 (4)	-0.1092 (4)	0.0194 (9)
C6	0.1581 (4)	0.0118 (5)	0.0671 (5)	0.0215 (9)
H6	0.084911	0.035530	0.018411	0.026*
C7	0.1483 (4)	-0.0844 (4)	0.1798 (4)	0.0188 (9)
C8	0.2501 (3)	-0.1470 (4)	0.2449 (6)	0.0215 (9)
H8	0.333133	-0.132248	0.214145	0.026*
C9	0.2277 (4)	-0.2306 (4)	0.3544 (5)	0.0208 (9)
H9	0.295199	-0.273712	0.400284	0.025*
C10	0.1052 (4)	-0.2507 (5)	0.3966 (5)	0.0228 (10)
H10	0.091113	-0.306383	0.473419	0.027*
C11	0.0286 (3)	-0.1154 (4)	0.2275 (5)	0.0196 (9)
H11	-0.041192	-0.077506	0.181272	0.023*
N1	0.2581 (3)	0.1569 (4)	-0.0731 (4)	0.0196 (8)
H1N	0.186 (4)	0.181 (5)	-0.107 (5)	0.023*
N2	0.2634 (3)	0.0646 (4)	0.0328 (4)	0.0211 (8)
N3	0.0061 (3)	-0.1955 (4)	0.3344 (4)	0.0217 (8)
O1	0.4666 (3)	0.2073 (3)	-0.0557 (4)	0.0278 (8)
S1	0.48271 (9)	0.42487 (11)	-0.25732 (14)	0.0248 (3)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.030 (2)	0.024 (2)	0.022 (3)	-0.0009 (18)	0.009 (2)	0.002 (2)
C2	0.030 (2)	0.026 (2)	0.016 (3)	0.0038 (18)	0.000 (2)	0.006 (2)
C3	0.026 (2)	0.022 (2)	0.022 (3)	0.0033 (16)	-0.0001 (18)	0.0045 (19)
C4	0.025 (2)	0.0204 (19)	0.015 (2)	0.0014 (16)	-0.0012 (18)	-0.0021 (17)
C5	0.020 (2)	0.022 (2)	0.017 (2)	-0.0029 (16)	0.0016 (18)	-0.0019 (19)
C6	0.0196 (19)	0.025 (2)	0.019 (2)	-0.0002 (17)	-0.004 (2)	-0.0007 (19)
C7	0.018 (2)	0.0216 (19)	0.017 (2)	-0.0014 (15)	0.0001 (18)	-0.0027 (18)
C8	0.0177 (18)	0.0242 (19)	0.023 (2)	-0.0026 (13)	-0.002 (3)	-0.005 (2)
C9	0.020 (2)	0.026 (2)	0.017 (2)	0.0002 (16)	-0.006 (2)	0.001 (2)
C10	0.025 (2)	0.027 (2)	0.017 (2)	0.0016 (17)	-0.001 (2)	-0.0001 (19)

C11	0.0169 (17)	0.0238 (18)	0.018 (2)	0.0012 (14)	-0.001 (2)	-0.002 (2)
N1	0.0164 (17)	0.0258 (18)	0.016 (2)	-0.0001 (14)	-0.0040 (16)	0.0038 (16)
N2	0.0247 (19)	0.0223 (18)	0.016 (2)	-0.0014 (14)	-0.0010 (18)	0.0000 (16)
N3	0.0250 (18)	0.0222 (16)	0.018 (2)	0.0005 (15)	0.0031 (17)	-0.0009 (16)
O1	0.0179 (15)	0.0385 (18)	0.0270 (19)	-0.0039 (12)	-0.0050 (15)	0.0063 (17)
S1	0.0222 (5)	0.0301 (5)	0.0221 (6)	-0.0036 (4)	0.0015 (6)	0.0037 (6)

Geometric parameters (Å, °)

C1—C2	1.364 (6)	C6—H6	0.9500
C1—S1	1.708 (5)	C7—C11	1.398 (5)
C1—H1	0.9500	C7—C8	1.403 (6)
C2—C3	1.415 (6)	C8—C9	1.381 (7)
C2—H2	0.9500	C8—H8	0.9500
C3—C4	1.363 (6)	C9—C10	1.390 (6)
C3—H3	0.9500	C9—H9	0.9500
C4—C5	1.479 (6)	C10—N3	1.338 (5)
C4—S1	1.729 (4)	C10—H10	0.9500
C5—O1	1.230 (5)	C11—N3	1.342 (6)
C5—N1	1.360 (5)	C11—H11	0.9500
C6—N2	1.280 (5)	N1—N2	1.384 (5)
C6—C7	1.463 (6)	N1—H1N	0.87 (5)
C2—C1—S1	111.6 (3)	C8—C7—C6	125.0 (4)
C2—C1—H1	124.2	C9—C8—C7	118.9 (4)
S1—C1—H1	124.2	C9—C8—H8	120.5
C1—C2—C3	112.7 (4)	C7—C8—H8	120.5
C1—C2—H2	123.7	C8—C9—C10	119.2 (4)
C3—C2—H2	123.7	C8—C9—H9	120.4
C4—C3—C2	112.9 (4)	C10—C9—H9	120.4
C4—C3—H3	123.5	N3—C10—C9	123.2 (4)
C2—C3—H3	123.5	N3—C10—H10	118.4
C3—C4—C5	133.3 (4)	C9—C10—H10	118.4
C3—C4—S1	110.8 (3)	N3—C11—C7	124.1 (4)
C5—C4—S1	115.9 (3)	N3—C11—H11	118.0
O1—C5—N1	123.7 (4)	C7—C11—H11	118.0
O1—C5—C4	120.6 (4)	C5—N1—N2	118.5 (4)
N1—C5—C4	115.7 (4)	C5—N1—H1N	120 (3)
N2—C6—C7	121.1 (4)	N2—N1—H1N	120 (3)
N2—C6—H6	119.4	C6—N2—N1	114.8 (4)
C7—C6—H6	119.4	C10—N3—C11	117.3 (4)
C11—C7—C8	117.3 (4)	C1—S1—C4	92.0 (2)
C11—C7—C6	117.7 (4)		
S1—C1—C2—C3	0.2 (5)	C8—C9—C10—N3	1.6 (7)
C1—C2—C3—C4	-0.3 (6)	C8—C7—C11—N3	3.2 (6)
C2—C3—C4—C5	-179.1 (5)	C6—C7—C11—N3	-176.2 (4)
C2—C3—C4—S1	0.2 (5)	O1—C5—N1—N2	2.4 (6)

C3—C4—C5—O1	174.4 (5)	C4—C5—N1—N2	-177.6 (3)
S1—C4—C5—O1	-4.9 (6)	C7—C6—N2—N1	-178.2 (4)
C3—C4—C5—N1	-5.6 (7)	C5—N1—N2—C6	175.1 (4)
S1—C4—C5—N1	175.1 (3)	C9—C10—N3—C11	-1.0 (6)
N2—C6—C7—C11	167.6 (4)	C7—C11—N3—C10	-1.5 (6)
N2—C6—C7—C8	-11.8 (7)	C2—C1—S1—C4	-0.1 (4)
C11—C7—C8—C9	-2.5 (6)	C3—C4—S1—C1	-0.1 (4)
C6—C7—C8—C9	176.9 (4)	C5—C4—S1—C1	179.4 (3)
C7—C8—C9—C10	0.3 (6)		

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>
N1—H1 <i>N</i> ...N3 ⁱ	0.87 (5)	2.14 (5)	2.995 (5)	166 (4)
C1—H1...O1 ⁱⁱ	0.95	2.53	3.471 (6)	171
C3—H3...N3 ⁱ	0.95	2.61	3.479 (6)	152
C6—H6...N3 ⁱ	0.95	2.59	3.410 (6)	145
C9—H9...O1 ⁱⁱⁱ	0.95	2.66	3.397 (5)	135
C11—H11...N2 ^{iv}	0.95	2.57	3.481 (6)	160

Symmetry codes: (i) $-x, -y, z-1/2$; (ii) $-x+1, -y+1, z-1/2$; (iii) $-x+1, -y, z+1/2$; (iv) $x-1/2, -y, z$.*N'*-'[(*E*)-Pyridin-2-ylmethylidene]thiophene-2-carbohydrazide (II)

Crystal data

C₁₁H₉N₃OS $M_r = 231.27$ Orthorhombic, *Pna*2₁ $a = 18.4056$ (13) Å $b = 9.5255$ (7) Å $c = 6.0300$ (4) Å $V = 1057.19$ (13) Å³ $Z = 4$ $F(000) = 480$ $D_x = 1.453$ Mg m⁻³Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 6000 reflections

 $\theta = 2.4$ – 27.5° $\mu = 0.29$ mm⁻¹ $T = 100$ K

Blade, dark orange

0.15 × 0.06 × 0.04 mm

Data collection

Rigaku Saturn724+ CCD
diffractometer ω scansAbsorption correction: multi-scan
(CrystalClear; Rigaku, 2012) $T_{\min} = 0.756$, $T_{\max} = 1.000$

7314 measured reflections

1979 independent reflections

1930 reflections with $I > 2\sigma(I)$ $R_{\text{int}} = 0.026$ $\theta_{\max} = 27.5^\circ$, $\theta_{\min} = 3.1^\circ$ $h = -23 \rightarrow 23$ $k = -9 \rightarrow 12$ $l = -5 \rightarrow 7$

Refinement

Refinement on F^2

Least-squares matrix: full

 $R[F^2 > 2\sigma(F^2)] = 0.029$ $wR(F^2) = 0.083$ $S = 1.08$

1979 reflections

148 parameters

1 restraint

Primary atom site location: structure-invariant
direct methods

Hydrogen site location: mixed

H atoms treated by a mixture of independent
and constrained refinement $w = 1/[\sigma^2(F_o^2) + (0.0573P)^2 + 0.2224P]$ where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\max} = 0.001$

$$\Delta\rho_{\max} = 0.33 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.24 \text{ e } \text{\AA}^{-3}$$

Absolute structure: Parsons *et al.* (2013)

Absolute structure parameter: 0.04 (4)

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)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.80728 (12)	0.2567 (2)	0.9079 (4)	0.0243 (5)
H1	0.844507	0.190518	0.876806	0.029*
C2	0.80182 (12)	0.3272 (2)	1.1043 (4)	0.0240 (5)
H2	0.834112	0.312980	1.225101	0.029*
C3	0.74255 (10)	0.4248 (2)	1.1102 (5)	0.0225 (5)
H3	0.730933	0.483815	1.232138	0.027*
C4	0.70395 (11)	0.4200 (2)	0.9075 (4)	0.0198 (4)
C5	0.64198 (11)	0.5159 (2)	0.8639 (4)	0.0201 (4)
C6	0.56443 (11)	0.3875 (2)	0.3737 (4)	0.0214 (4)
H6	0.530355	0.461814	0.358627	0.026*
C7	0.56402 (10)	0.2730 (2)	0.2119 (5)	0.0207 (4)
C8	0.61299 (11)	0.1601 (2)	0.2192 (5)	0.0248 (4)
H8	0.647838	0.152750	0.334814	0.030*
C9	0.60922 (12)	0.0599 (2)	0.0540 (5)	0.0282 (5)
H9	0.642008	-0.017145	0.053144	0.034*
C10	0.55693 (12)	0.0730 (2)	-0.1110 (5)	0.0276 (5)
H10	0.553393	0.005274	-0.226127	0.033*
C11	0.51001 (12)	0.1869 (2)	-0.1042 (5)	0.0252 (5)
H11	0.474376	0.195559	-0.217400	0.030*
N1	0.60295 (9)	0.50362 (19)	0.6733 (3)	0.0207 (4)
H1N	0.5663 (14)	0.573 (3)	0.629 (5)	0.025*
N2	0.60975 (9)	0.38992 (19)	0.5354 (3)	0.0200 (4)
N3	0.51261 (10)	0.2853 (2)	0.0546 (4)	0.0222 (4)
O1	0.62639 (9)	0.60967 (18)	0.9963 (3)	0.0263 (4)
S1	0.74058 (3)	0.29964 (5)	0.72453 (13)	0.02379 (16)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0204 (9)	0.0272 (11)	0.0252 (13)	0.0009 (8)	-0.0035 (9)	-0.0004 (11)
C2	0.0236 (10)	0.0273 (10)	0.0209 (12)	-0.0006 (9)	-0.0040 (9)	-0.0004 (10)
C3	0.0180 (9)	0.0194 (9)	0.0302 (14)	0.0013 (7)	0.0020 (9)	0.0050 (10)
C4	0.0203 (8)	0.0214 (9)	0.0177 (11)	-0.0019 (7)	0.0025 (8)	0.0003 (9)
C5	0.0201 (9)	0.0217 (9)	0.0184 (11)	-0.0016 (7)	0.0022 (8)	0.0005 (9)
C6	0.0180 (8)	0.0250 (10)	0.0213 (11)	0.0017 (7)	-0.0001 (9)	-0.0007 (9)
C7	0.0177 (8)	0.0244 (10)	0.0200 (11)	-0.0014 (7)	-0.0005 (10)	0.0021 (11)
C8	0.0205 (9)	0.0279 (10)	0.0258 (12)	0.0017 (7)	-0.0027 (10)	0.0002 (12)

C9	0.0268 (10)	0.0272 (11)	0.0307 (14)	0.0061 (9)	0.0010 (10)	-0.0019 (11)
C10	0.0275 (10)	0.0281 (11)	0.0271 (14)	-0.0002 (9)	0.0022 (10)	-0.0066 (10)
C11	0.0221 (9)	0.0306 (11)	0.0229 (13)	0.0000 (8)	-0.0032 (10)	-0.0009 (10)
N1	0.0199 (8)	0.0231 (8)	0.0189 (11)	0.0017 (7)	0.0003 (7)	-0.0012 (8)
N2	0.0181 (7)	0.0239 (8)	0.0178 (9)	-0.0005 (6)	0.0010 (7)	0.0006 (8)
N3	0.0202 (8)	0.0262 (9)	0.0203 (11)	0.0011 (6)	-0.0014 (8)	-0.0003 (8)
O1	0.0283 (8)	0.0284 (8)	0.0222 (10)	0.0038 (6)	-0.0002 (7)	-0.0046 (7)
S1	0.0226 (2)	0.0288 (3)	0.0200 (3)	0.00348 (18)	-0.0016 (3)	-0.0026 (3)

Geometric parameters (Å, °)

C1—C2	1.365 (4)	C6—H6	0.9500
C1—S1	1.702 (2)	C7—N3	1.345 (3)
C1—H1	0.9500	C7—C8	1.404 (3)
C2—C3	1.434 (3)	C8—C9	1.381 (4)
C2—H2	0.9500	C8—H8	0.9500
C3—C4	1.415 (3)	C9—C10	1.390 (4)
C3—H3	0.9500	C9—H9	0.9500
C4—C5	1.485 (3)	C10—C11	1.387 (3)
C4—S1	1.728 (2)	C10—H10	0.9500
C5—O1	1.232 (3)	C11—N3	1.341 (3)
C5—N1	1.361 (3)	C11—H11	0.9500
C6—N2	1.284 (3)	N1—N2	1.371 (3)
C6—C7	1.463 (3)	N1—H1N	0.98 (3)
C2—C1—S1	113.11 (17)	C8—C7—C6	123.1 (2)
C2—C1—H1	123.4	C9—C8—C7	118.3 (2)
S1—C1—H1	123.4	C9—C8—H8	120.8
C1—C2—C3	113.4 (2)	C7—C8—H8	120.8
C1—C2—H2	123.3	C8—C9—C10	119.3 (2)
C3—C2—H2	123.3	C8—C9—H9	120.4
C4—C3—C2	109.9 (2)	C10—C9—H9	120.4
C4—C3—H3	125.1	C11—C10—C9	118.7 (2)
C2—C3—H3	125.1	C11—C10—H10	120.6
C3—C4—C5	121.3 (2)	C9—C10—H10	120.6
C3—C4—S1	112.16 (16)	N3—C11—C10	123.0 (2)
C5—C4—S1	126.50 (18)	N3—C11—H11	118.5
O1—C5—N1	119.15 (19)	C10—C11—H11	118.5
O1—C5—C4	120.7 (2)	C5—N1—N2	122.15 (18)
N1—C5—C4	120.1 (2)	C5—N1—H1N	122.2 (17)
N2—C6—C7	121.55 (19)	N2—N1—H1N	115.5 (17)
N2—C6—H6	119.2	C6—N2—N1	114.55 (19)
C7—C6—H6	119.2	C11—N3—C7	117.90 (19)
N3—C7—C8	122.7 (2)	C1—S1—C4	91.48 (12)
N3—C7—C6	114.14 (18)		
S1—C1—C2—C3	-1.8 (3)	C8—C9—C10—C11	0.0 (4)
C1—C2—C3—C4	1.0 (3)	C9—C10—C11—N3	-0.1 (4)

C2—C3—C4—C5	-176.80 (19)	O1—C5—N1—N2	-169.81 (19)
C2—C3—C4—S1	0.2 (2)	C4—C5—N1—N2	12.0 (3)
C3—C4—C5—O1	5.8 (3)	C7—C6—N2—N1	-179.61 (19)
S1—C4—C5—O1	-170.67 (17)	C5—N1—N2—C6	173.74 (19)
C3—C4—C5—N1	-176.02 (19)	C10—C11—N3—C7	1.0 (3)
S1—C4—C5—N1	7.5 (3)	C8—C7—N3—C11	-1.9 (3)
N2—C6—C7—N3	179.2 (2)	C6—C7—N3—C11	178.0 (2)
N2—C6—C7—C8	-1.0 (4)	C2—C1—S1—C4	1.60 (19)
N3—C7—C8—C9	1.8 (4)	C3—C4—S1—C1	-0.99 (17)
C6—C7—C8—C9	-178.0 (2)	C5—C4—S1—C1	175.80 (19)
C7—C8—C9—C10	-0.8 (4)		

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>
N1—H1N...N3 ⁱ	0.98 (3)	2.03 (3)	3.013 (3)	177 (3)
C1—H1...O1 ⁱⁱ	0.95	2.48	3.101 (3)	123
C2—H2...O1 ⁱⁱⁱ	0.95	2.64	3.410 (3)	139

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

N-Methyl-*N'*-[(*E*)-pyridin-2-ylmethylidene]thiophene-2-carbohydrazide (III)

Crystal data

C₁₂H₁₁N₃OS

M_r = 245.30

Monoclinic, *C2/c*

a = 21.0690 (15) Å

b = 5.1085 (4) Å

c = 21.1531 (15) Å

β = 95.265 (2)°

V = 2267.1 (3) Å³

Z = 8

F(000) = 1024

D_x = 1.437 Mg m⁻³

Mo *K*α radiation, λ = 0.71073 Å

Cell parameters from 7400 reflections

θ = 2.9–27.5°

μ = 0.27 mm⁻¹

T = 100 K

Lath, colourless

0.42 × 0.12 × 0.03 mm

Data collection

Rigaku Saturn724+ CCD
diffractometer

ω scans

Absorption correction: multi-scan
(CrystalClear; Rigaku, 2012)

T_{min} = 0.780, *T_{max}* = 1.000

8717 measured reflections

2563 independent reflections

2307 reflections with *I* > 2σ(*I*)

R_{int} = 0.022

θ_{max} = 27.5°, θ_{min} = 2.9°

h = -27→27

k = -6→6

l = -27→21

Refinement

Refinement on *F*²

Least-squares matrix: full

R[*F*² > 2σ(*F*²)] = 0.031

wR(*F*²) = 0.087

S = 1.07

2563 reflections

155 parameters

0 restraints

Primary atom site location: structure-invariant
direct methods

Hydrogen site location: inferred from
neighbouring sites

H-atom parameters constrained

w = 1/[σ²(*F_o*²) + (0.0408*P*)² + 2.1991*P*]

where *P* = (*F_o*² + 2*F_c*²)/3

(Δ/σ)_{max} = 0.001

$$\Delta\rho_{\max} = 0.33 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.29 \text{ e } \text{\AA}^{-3}$$

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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.50199 (7)	0.8774 (3)	0.34463 (7)	0.0262 (3)
H1	0.525890	0.988871	0.319795	0.031*
C2	0.50475 (7)	0.8871 (3)	0.40904 (7)	0.0283 (3)
H2	0.530839	1.006088	0.434266	0.034*
C3	0.46445 (6)	0.7003 (3)	0.43432 (6)	0.0243 (3)
H3	0.460459	0.680014	0.478420	0.029*
C4	0.43135 (6)	0.5499 (3)	0.38752 (6)	0.0196 (3)
C5	0.38600 (6)	0.3464 (3)	0.40503 (6)	0.0206 (3)
C6	0.30541 (6)	0.0098 (3)	0.37672 (6)	0.0229 (3)
H6A	0.306676	0.001379	0.423104	0.034*
H6B	0.316415	-0.161776	0.360136	0.034*
H6C	0.262463	0.059115	0.359010	0.034*
C7	0.32615 (6)	0.1249 (3)	0.25363 (6)	0.0190 (3)
H7	0.298098	-0.007769	0.265792	0.023*
C8	0.33189 (6)	0.1729 (2)	0.18583 (6)	0.0178 (3)
C9	0.36845 (6)	0.3762 (3)	0.16384 (6)	0.0197 (3)
H9	0.392055	0.489970	0.192720	0.024*
C10	0.36941 (6)	0.4078 (3)	0.09876 (6)	0.0222 (3)
H10	0.393440	0.545017	0.082220	0.027*
C11	0.33481 (7)	0.2364 (3)	0.05837 (6)	0.0247 (3)
H11	0.334717	0.253470	0.013642	0.030*
C12	0.30036 (7)	0.0398 (3)	0.08438 (6)	0.0266 (3)
H12	0.277110	-0.078189	0.056315	0.032*
N1	0.35096 (5)	0.2040 (2)	0.35878 (5)	0.0194 (2)
N2	0.35836 (5)	0.2591 (2)	0.29655 (5)	0.0176 (2)
N3	0.29791 (6)	0.0063 (2)	0.14694 (5)	0.0234 (3)
O1	0.37945 (5)	0.3068 (2)	0.46105 (4)	0.0291 (2)
S1	0.45075 (2)	0.64215 (7)	0.31337 (2)	0.02308 (11)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0201 (7)	0.0236 (7)	0.0350 (8)	-0.0028 (6)	0.0027 (5)	-0.0049 (6)
C2	0.0219 (7)	0.0273 (7)	0.0349 (8)	0.0015 (6)	-0.0020 (6)	-0.0129 (6)
C3	0.0227 (7)	0.0279 (7)	0.0223 (6)	0.0052 (6)	0.0015 (5)	-0.0055 (5)
C4	0.0183 (6)	0.0220 (6)	0.0185 (6)	0.0042 (5)	0.0015 (5)	-0.0022 (5)
C5	0.0210 (6)	0.0229 (6)	0.0180 (6)	0.0061 (5)	0.0026 (5)	-0.0006 (5)
C6	0.0203 (6)	0.0253 (7)	0.0234 (6)	-0.0005 (6)	0.0038 (5)	0.0070 (5)

C7	0.0185 (6)	0.0182 (6)	0.0204 (6)	0.0001 (5)	0.0031 (5)	0.0018 (5)
C8	0.0167 (6)	0.0178 (6)	0.0188 (6)	0.0023 (5)	0.0010 (4)	-0.0002 (5)
C9	0.0181 (6)	0.0218 (6)	0.0191 (6)	-0.0008 (5)	0.0010 (5)	-0.0009 (5)
C10	0.0216 (6)	0.0239 (7)	0.0218 (6)	-0.0010 (5)	0.0049 (5)	0.0010 (5)
C11	0.0293 (7)	0.0281 (7)	0.0171 (6)	0.0017 (6)	0.0042 (5)	-0.0019 (5)
C12	0.0335 (8)	0.0240 (7)	0.0218 (6)	-0.0036 (6)	0.0006 (5)	-0.0061 (5)
N1	0.0189 (5)	0.0237 (6)	0.0158 (5)	-0.0006 (4)	0.0024 (4)	0.0035 (4)
N2	0.0175 (5)	0.0200 (5)	0.0155 (5)	0.0018 (4)	0.0024 (4)	0.0020 (4)
N3	0.0281 (6)	0.0200 (6)	0.0218 (5)	-0.0030 (5)	0.0008 (4)	-0.0022 (4)
O1	0.0378 (6)	0.0339 (6)	0.0161 (4)	0.0009 (5)	0.0051 (4)	0.0002 (4)
S1	0.02249 (19)	0.02627 (19)	0.02056 (18)	-0.00532 (13)	0.00245 (12)	-0.00153 (12)

Geometric parameters (Å, °)

C1—C2	1.359 (2)	C7—N2	1.2815 (17)
C1—S1	1.7075 (14)	C7—C8	1.4709 (17)
C1—H1	0.9500	C7—H7	0.9500
C2—C3	1.414 (2)	C8—N3	1.3436 (17)
C2—H2	0.9500	C8—C9	1.3981 (18)
C3—C4	1.3894 (19)	C9—C10	1.3879 (18)
C3—H3	0.9500	C9—H9	0.9500
C4—C5	1.4817 (19)	C10—C11	1.3835 (19)
C4—S1	1.7223 (13)	C10—H10	0.9500
C5—O1	1.2225 (16)	C11—C12	1.382 (2)
C5—N1	1.3780 (17)	C11—H11	0.9500
C6—N1	1.4545 (17)	C12—N3	1.3400 (17)
C6—H6A	0.9800	C12—H12	0.9500
C6—H6B	0.9800	N1—N2	1.3690 (14)
C6—H6C	0.9800		
C2—C1—S1	112.41 (11)	C8—C7—H7	119.5
C2—C1—H1	123.8	N3—C8—C9	123.07 (11)
S1—C1—H1	123.8	N3—C8—C7	113.86 (11)
C1—C2—C3	112.48 (13)	C9—C8—C7	123.06 (11)
C1—C2—H2	123.8	C10—C9—C8	118.36 (12)
C3—C2—H2	123.8	C10—C9—H9	120.8
C4—C3—C2	112.53 (12)	C8—C9—H9	120.8
C4—C3—H3	123.7	C11—C10—C9	118.95 (13)
C2—C3—H3	123.7	C11—C10—H10	120.5
C3—C4—C5	120.19 (12)	C9—C10—H10	120.5
C3—C4—S1	110.61 (10)	C12—C11—C10	118.69 (12)
C5—C4—S1	129.19 (10)	C12—C11—H11	120.7
O1—C5—N1	120.00 (13)	C10—C11—H11	120.7
O1—C5—C4	119.42 (12)	N3—C12—C11	123.71 (13)
N1—C5—C4	120.58 (11)	N3—C12—H12	118.1
N1—C6—H6A	109.5	C11—C12—H12	118.1
N1—C6—H6B	109.5	N2—N1—C5	118.24 (11)
H6A—C6—H6B	109.5	N2—N1—C6	121.81 (11)

N1—C6—H6C	109.5	C5—N1—C6	119.89 (11)
H6A—C6—H6C	109.5	C7—N2—N1	118.14 (11)
H6B—C6—H6C	109.5	C12—N3—C8	117.20 (12)
N2—C7—C8	121.06 (12)	C1—S1—C4	91.97 (7)
N2—C7—H7	119.5		
S1—C1—C2—C3	-0.08 (16)	C10—C11—C12—N3	0.7 (2)
C1—C2—C3—C4	0.02 (18)	O1—C5—N1—N2	178.23 (11)
C2—C3—C4—C5	-179.06 (12)	C4—C5—N1—N2	-1.19 (18)
C2—C3—C4—S1	0.04 (15)	O1—C5—N1—C6	1.06 (19)
C3—C4—C5—O1	-2.21 (19)	C4—C5—N1—C6	-178.37 (11)
S1—C4—C5—O1	178.88 (10)	C8—C7—N2—N1	-179.79 (11)
C3—C4—C5—N1	177.22 (12)	C5—N1—N2—C7	179.40 (12)
S1—C4—C5—N1	-1.69 (19)	C6—N1—N2—C7	-3.49 (18)
N2—C7—C8—N3	176.35 (12)	C11—C12—N3—C8	-1.0 (2)
N2—C7—C8—C9	-4.8 (2)	C9—C8—N3—C12	0.5 (2)
N3—C8—C9—C10	0.3 (2)	C7—C8—N3—C12	179.38 (12)
C7—C8—C9—C10	-178.51 (12)	C2—C1—S1—C4	0.09 (12)
C8—C9—C10—C11	-0.6 (2)	C3—C4—S1—C1	-0.07 (11)
C9—C10—C11—C12	0.1 (2)	C5—C4—S1—C1	178.92 (13)

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C9—H9 \cdots S1	0.95	2.84	3.7217 (13)	155
C6—H6C \cdots N3 ⁱ	0.98	2.61	3.3499 (18)	132

Symmetry code: (i) $-x+1/2, y+1/2, -z+1/2$.*N'*-[(*E*)-Pyridin-2-ylmethylidene]-2-(thiophen-2-yl)ethanohydrazide (IV)

Crystal data

 $C_{12}H_{11}N_3OS$ $M_r = 245.30$ Monoclinic, $P2_1/c$ $a = 11.3963$ (8) \AA $b = 9.2782$ (7) \AA $c = 11.8178$ (8) \AA $\beta = 112.761$ (2) $^\circ$ $V = 1152.27$ (14) \AA^3 $Z = 4$ $F(000) = 512$ $D_x = 1.414$ Mg m^{-3} Mo $K\alpha$ radiation, $\lambda = 0.71073$ \AA

Cell parameters from 43879 reflections

 $\theta = 2.9\text{--}27.5^\circ$ $\mu = 0.27$ mm^{-1} $T = 100$ K

Block, colourless

 $0.10 \times 0.09 \times 0.06$ mm

Data collection

Rigaku AFC12 CCD
diffractometer ω scansAbsorption correction: multi-scan
(CrystalClear; Rigaku, 2012) $T_{\min} = 0.723$, $T_{\max} = 1.000$

8155 measured reflections

2593 independent reflections

2138 reflections with $I > 2\sigma(I)$ $R_{\text{int}} = 0.031$ $\theta_{\max} = 28.4^\circ$, $\theta_{\min} = 2.9^\circ$ $h = -15 \rightarrow 14$ $k = -12 \rightarrow 11$ $l = -14 \rightarrow 14$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.041$
 $wR(F^2) = 0.112$
 $S = 1.10$
 2593 reflections
 170 parameters
 10 restraints

Primary atom site location: structure-invariant
 direct methods
 Hydrogen site location: mixed
 H atoms treated by a mixture of independent
 and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0505P)^2 + 0.7045P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.32 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.30 \text{ e } \text{\AA}^{-3}$

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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
C1	0.9466 (2)	0.7136 (3)	0.2749 (2)	0.0222 (5)	0.851 (2)
H1	1.033688	0.689483	0.317920	0.027*	0.851 (2)
C2	0.8750 (2)	0.6617 (3)	0.1571 (2)	0.0203 (5)	0.851 (2)
H2	0.905946	0.598307	0.111806	0.024*	0.851 (2)
C3	0.7527 (8)	0.7158 (11)	0.1161 (7)	0.0246 (10)	0.851 (2)
H3	0.689801	0.695835	0.037087	0.029*	0.851 (2)
C4	0.73066 (15)	0.80326 (17)	0.20255 (15)	0.0211 (3)	0.851 (2)
S1	0.86521 (5)	0.82422 (7)	0.33564 (5)	0.02360 (18)	0.851 (2)
C1B	0.8982 (14)	0.684 (2)	0.1833 (17)	0.0203 (5)	0.149 (2)
H1B	0.956589	0.632055	0.158977	0.024*	0.149 (2)
C2B	0.9327 (13)	0.7537 (17)	0.2944 (14)	0.0222 (5)	0.149 (2)
H2B	1.015819	0.750408	0.356806	0.027*	0.149 (2)
C3B	0.8327 (13)	0.829 (2)	0.3049 (14)	0.02360 (18)	0.149 (2)
H3B	0.836035	0.888345	0.371821	0.028*	0.149 (2)
C4B	0.73066 (15)	0.80326 (17)	0.20255 (15)	0.0211 (3)	0.149 (2)
S1B	0.7385 (12)	0.6996 (17)	0.0929 (12)	0.0246 (10)	0.149 (2)
C5	0.61018 (15)	0.86577 (18)	0.19459 (16)	0.0231 (3)	
H5A	0.553207	0.878920	0.107425	0.028*	
H5B	0.625573	0.961417	0.234861	0.028*	
C6	0.54702 (14)	0.76587 (17)	0.25759 (15)	0.0206 (3)	
C7	0.35889 (15)	0.83579 (18)	0.42527 (15)	0.0223 (3)	
H7	0.359384	0.937962	0.420223	0.027*	
C8	0.28771 (14)	0.76417 (18)	0.49016 (15)	0.0207 (3)	
C9	0.27577 (15)	0.61405 (19)	0.49162 (16)	0.0243 (4)	
H9	0.314773	0.554343	0.450832	0.029*	
C10	0.20629 (15)	0.55382 (19)	0.55336 (16)	0.0271 (4)	
H10	0.197174	0.452251	0.556146	0.033*	
C11	0.14999 (16)	0.64555 (19)	0.61139 (16)	0.0260 (4)	
H11	0.101007	0.607862	0.653853	0.031*	

C12	0.16714 (16)	0.79323 (19)	0.60568 (17)	0.0267 (4)
H12	0.129255	0.854810	0.646226	0.032*
N1	0.48282 (13)	0.83765 (15)	0.31638 (13)	0.0211 (3)
H1N	0.4714 (18)	0.932 (2)	0.3080 (18)	0.025*
N2	0.42014 (12)	0.76009 (15)	0.37563 (13)	0.0213 (3)
N3	0.23384 (13)	0.85429 (16)	0.54651 (13)	0.0247 (3)
O1	0.55355 (11)	0.63460 (13)	0.25449 (13)	0.0280 (3)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0172 (8)	0.0271 (13)	0.0254 (12)	0.0030 (8)	0.0118 (7)	0.0006 (9)
C2	0.0203 (11)	0.0209 (13)	0.0221 (14)	-0.0002 (9)	0.0109 (10)	-0.0036 (8)
C3	0.0205 (18)	0.024 (2)	0.028 (3)	-0.0032 (14)	0.0080 (19)	-0.0029 (17)
C4	0.0196 (7)	0.0194 (7)	0.0245 (8)	-0.0023 (6)	0.0088 (6)	0.0032 (6)
S1	0.0191 (3)	0.0280 (3)	0.0230 (3)	-0.0014 (2)	0.0073 (2)	-0.0037 (2)
C1B	0.0203 (11)	0.0209 (13)	0.0221 (14)	-0.0002 (9)	0.0109 (10)	-0.0036 (8)
C2B	0.0172 (8)	0.0271 (13)	0.0254 (12)	0.0030 (8)	0.0118 (7)	0.0006 (9)
C3B	0.0191 (3)	0.0280 (3)	0.0230 (3)	-0.0014 (2)	0.0073 (2)	-0.0037 (2)
C4B	0.0196 (7)	0.0194 (7)	0.0245 (8)	-0.0023 (6)	0.0088 (6)	0.0032 (6)
S1B	0.0205 (18)	0.024 (2)	0.028 (3)	-0.0032 (14)	0.0080 (19)	-0.0029 (17)
C5	0.0204 (7)	0.0176 (7)	0.0319 (9)	-0.0002 (6)	0.0108 (6)	0.0024 (7)
C6	0.0164 (6)	0.0194 (8)	0.0244 (8)	-0.0001 (6)	0.0061 (6)	0.0011 (6)
C7	0.0219 (7)	0.0192 (8)	0.0251 (8)	0.0000 (6)	0.0083 (6)	0.0006 (6)
C8	0.0181 (7)	0.0218 (8)	0.0211 (8)	0.0005 (6)	0.0064 (6)	-0.0013 (6)
C9	0.0212 (7)	0.0231 (8)	0.0298 (9)	0.0009 (6)	0.0112 (6)	-0.0033 (7)
C10	0.0224 (7)	0.0222 (8)	0.0354 (10)	-0.0002 (6)	0.0098 (7)	0.0021 (7)
C11	0.0239 (7)	0.0267 (9)	0.0286 (9)	-0.0009 (6)	0.0114 (7)	0.0032 (7)
C12	0.0273 (8)	0.0277 (9)	0.0300 (9)	0.0014 (7)	0.0163 (7)	-0.0025 (7)
N1	0.0213 (6)	0.0168 (6)	0.0271 (7)	0.0006 (5)	0.0114 (6)	0.0015 (5)
N2	0.0183 (6)	0.0211 (7)	0.0244 (7)	-0.0007 (5)	0.0081 (5)	0.0013 (5)
N3	0.0247 (6)	0.0225 (7)	0.0290 (8)	0.0012 (5)	0.0128 (6)	-0.0003 (6)
O1	0.0267 (6)	0.0161 (6)	0.0475 (8)	-0.0002 (5)	0.0214 (6)	0.0000 (5)

Geometric parameters (Å, °)

C1—C2	1.399 (3)	C5—H5A	0.9900
C1—S1	1.716 (2)	C5—H5B	0.9900
C1—H1	0.9500	C6—O1	1.222 (2)
C2—C3	1.380 (8)	C6—N1	1.362 (2)
C2—H2	0.9500	C7—N2	1.281 (2)
C3—C4	1.401 (7)	C7—C8	1.473 (2)
C3—H3	0.9500	C7—H7	0.9500
C4—C5	1.460 (2)	C8—N3	1.355 (2)
C4—S1	1.7311 (16)	C8—C9	1.400 (2)
C1B—C2B	1.379 (15)	C9—C10	1.385 (2)
C1B—S1B	1.723 (16)	C9—H9	0.9500
C1B—H1B	0.9500	C10—C11	1.395 (2)

C2B—C3B	1.384 (15)	C10—H10	0.9500
C2B—H2B	0.9500	C11—C12	1.389 (2)
C3B—C4B	1.337 (13)	C11—H11	0.9500
C3B—H3B	0.9500	C12—N3	1.341 (2)
C4B—C5	1.460 (2)	C12—H12	0.9500
C4B—S1B	1.643 (11)	N1—N2	1.3804 (19)
C5—C6	1.532 (2)	N1—H1N	0.88 (2)
C2—C1—S1	114.85 (18)	C4—C5—H5B	109.8
C2—C1—H1	122.6	C6—C5—H5B	109.8
S1—C1—H1	122.6	H5A—C5—H5B	108.2
C3—C2—C1	110.2 (3)	O1—C6—N1	123.63 (15)
C3—C2—H2	124.9	O1—C6—C5	122.90 (15)
C1—C2—H2	124.9	N1—C6—C5	113.47 (14)
C2—C3—C4	113.4 (5)	N2—C7—C8	119.90 (15)
C2—C3—H3	123.3	N2—C7—H7	120.1
C4—C3—H3	123.3	C8—C7—H7	120.1
C3—C4—C5	127.8 (3)	N3—C8—C9	122.90 (15)
C3—C4—S1	112.4 (3)	N3—C8—C7	115.03 (15)
C5—C4—S1	119.63 (13)	C9—C8—C7	122.07 (15)
C1—S1—C4	89.14 (10)	C10—C9—C8	119.07 (16)
C2B—C1B—S1B	113.1 (12)	C10—C9—H9	120.5
C2B—C1B—H1B	123.4	C8—C9—H9	120.5
S1B—C1B—H1B	123.4	C9—C10—C11	118.56 (16)
C1B—C2B—C3B	112.6 (13)	C9—C10—H10	120.7
C1B—C2B—H2B	123.7	C11—C10—H10	120.7
C3B—C2B—H2B	123.7	C12—C11—C10	118.53 (16)
C4B—C3B—C2B	106.5 (12)	C12—C11—H11	120.7
C4B—C3B—H3B	126.7	C10—C11—H11	120.7
C2B—C3B—H3B	126.7	N3—C12—C11	124.09 (16)
C3B—C4B—C5	117.0 (7)	N3—C12—H12	118.0
C3B—C4B—S1B	121.7 (7)	C11—C12—H12	118.0
C5—C4B—S1B	121.2 (4)	C6—N1—N2	119.30 (13)
C4B—S1B—C1B	85.9 (8)	C6—N1—H1N	120.7 (13)
C4B—C5—C6	109.60 (13)	N2—N1—H1N	119.4 (13)
C4—C5—C6	109.60 (13)	C7—N2—N1	115.27 (14)
C4—C5—H5A	109.8	C12—N3—C8	116.84 (15)
C6—C5—H5A	109.8		
S1—C1—C2—C3	1.1 (6)	C4B—C5—C6—O1	-35.6 (2)
C1—C2—C3—C4	-2.0 (9)	C4—C5—C6—O1	-35.6 (2)
C2—C3—C4—C5	-173.4 (4)	C4B—C5—C6—N1	144.72 (14)
C2—C3—C4—S1	2.1 (9)	C4—C5—C6—N1	144.72 (14)
C2—C1—S1—C4	0.1 (2)	N2—C7—C8—N3	175.58 (14)
C3—C4—S1—C1	-1.2 (5)	N2—C7—C8—C9	-5.2 (2)
C5—C4—S1—C1	174.74 (15)	N3—C8—C9—C10	-0.2 (2)
S1B—C1B—C2B—C3B	-4 (2)	C7—C8—C9—C10	-179.31 (15)
C1B—C2B—C3B—C4B	3 (2)	C8—C9—C10—C11	0.4 (2)

C2B—C3B—C4B—C5	176.8 (10)	C9—C10—C11—C12	-0.6 (2)
C2B—C3B—C4B—S1B	-0.5 (19)	C10—C11—C12—N3	0.7 (3)
C3B—C4B—S1B—C1B	-1.5 (16)	O1—C6—N1—N2	-0.5 (2)
C5—C4B—S1B—C1B	-178.7 (8)	C5—C6—N1—N2	179.18 (13)
C2B—C1B—S1B—C4B	3.1 (18)	C8—C7—N2—N1	179.54 (13)
C3B—C4B—C5—C6	-84.9 (10)	C6—N1—N2—C7	-177.90 (14)
S1B—C4B—C5—C6	92.4 (7)	C11—C12—N3—C8	-0.5 (3)
C3—C4—C5—C6	93.8 (6)	C9—C8—N3—C12	0.2 (2)
S1—C4—C5—C6	-81.44 (16)	C7—C8—N3—C12	179.39 (14)

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>
N1—H1N...O1 ⁱ	0.88 (2)	2.00 (2)	2.8628 (18)	164.9 (18)
C3—H3...N1 ⁱⁱ	0.95	2.78	3.718 (7)	172
C5—H5B...O1 ⁱ	0.99	2.64	3.307 (2)	125
C7—H7...S1B ⁱ	0.95	2.65	3.534 (16)	155
C12—H12...S1 ⁱⁱⁱ	0.95	2.98	3.6624 (19)	129

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