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

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The crystal structures of four thiophene–carbohydrazide–pyridine derivatives, viz. \(N'\)-[(E)-pyridin-3-ylmethylidene]thiophene-2-carbohydrazide, \(C_{11}H_{9}N_{3}OS\), (I), \(N'\)-[(E)-pyridin-2-ylmethylidene]thiophene-2-carbohydrazide, \(C_{11}H_{9}N_{3}OS\), (II), \(N\)-methyl-\(N'\)-[(E)-pyridin-2-ylmethylidene]thiophene-2-carbohydrazide, \(C_{12}H_{11}N_{3}OS\), (III) and \(N'\)-[(E)-pyridin-2-ylmethylidene]-2-(thiophen-2-yl)ethanohydrazide, \(C_{12}H_{11}N_{3}OS\), (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 \(N-H\cdot\cdot\cdot N_p\) hydrogen bonds in (I), which generate \((C7)\) chains propagating in the [001] direction; \(N-H\cdot\cdot\cdot N_p\) links also feature in (II), but in this case they lead to \((C6)\) [001] chains; in (IV), classical amide \((C4)\) \(N-H\cdot\cdot\cdot O\) links result in \([010]\) chains; in every case adjacent molecules in the chains are related by \(2_1\) screw axes. There are no classical hydrogen bonds in the extended structure of (III). Various weak \(C-H\cdot\cdot\cdot X\) \((X = O, N, S)\) interactions occur in each structure, but no aromatic \(\pi-\pi\) stacking is evident. The Hirshfeld surfaces and fingerprint plots for (I)–(IV) are compared.

1. Chemical context

Various thiophene–carbohydrazide derivatives containing a \(T-C(\equiv O)-NH-N=C=CH-R\) (\(T =\) 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, 2016a) 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., 2016b,c), we now describe the crystal structures and Hirshfeld surfaces of \(N'\)-[(E)-pyridin-3-ylmethylidene]thiophene-2-carbohydrazide, \(C_{11}H_{9}N_{3}OS\) (I), \(N'\)-[(E)-pyridin-2-ylmethylidene]thiophene-2-carbohydrazide, \(C_{11}H_{9}N_{3}OS\) (II), \(N\)-methyl-\(N'\)-[(E)-pyridin-2-ylmethylidene]thiophene-2-carbohydrazide, \(C_{12}H_{11}N_{3}OS\) (III) and \(N'\)-[(E)-pyridin-2-ylmethylidene]-2-(thiophen-2-yl)ethanohydrazide, \(C_{12}H_{11}N_{3}OS\) (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
methylene group inserted between the thiophene ring and the carboxyhydrazide 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 N2C6 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 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
between C9—H9 and S1 is 2.84 Å (C—H···S = 155°), 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 (~180° 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)°]. The dihedral angle between the aromatic rings (major disorder conformation for the thiophene moiety) in (IV) of 83.52 (13)° 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)°; C4—C5—C6—N1 = 144.72 (14)°].

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···N hydrogen bonds (double dashed lines). Symmetry codes: (i) −x, −y, z − ½; (ii) −x, −y, z + ½.

| Table 1 | Hydrogen-bond geometry (Å, °) for (I). |
| D—H···A | D—H | H···A | D····A | D—H···A |
| N1—H1N···N3’ | 0.87 (5) | 2.14 (5) | 2.995 (5) | 166 (4) |
| C1—H1···O1a | 0.95 | 2.53 | 3.471 (6) | 171 |
| C3—H3···N3’ | 0.95 | 2.61 | 3.479 (6) | 152 |
| C6—H6···N3’ | 0.95 | 2.59 | 3.410 (6) | 145 |
| C9—H9···O1’ | 0.95 | 2.66 | 3.397 (5) | 135 |
| C11—H11···N2’ | 0.95 | 2.57 | 3.481 (6) | 160 |

Symmetry codes: (i) −x, −y, z − ½; (ii) −x + 1, −y + 1, z − ½; (iii) −x + 1, −y, z + ½; (iv) x − ½, y + 1 − z, z + ½.

| Table 2 | Hydrogen-bond geometry (Å, °) for (II). |
| D—H···A | D—H | H···A | D····A | D—H···A |
| N1—H1N···N3’ | 0.98 (3) | 2.03 (3) | 3.013 (3) | 177 (3) |
| C1—H1···O1a | 0.95 | 2.48 | 3.101 (3) | 123 |
| C2—H2···O1’ | 0.95 | 2.64 | 3.410 (3) | 139 |

Symmetry codes: (i) −x + 1, −y + 1, z + ½; (ii) −x + 1, −y + 1, z − ½; (iii) −x + 1, −y + 1, z + ½.

| Table 3 | Hydrogen-bond geometry (Å, °) for (III). |
| D—H···A | D—H | H···A | D····A | D—H···A |
| C9—H9···S1 | 0.95 | 2.84 | 3.7217 (13) | 155 |
| C6—H6C···N3’ | 0.98 | 2.61 | 3.3499 (18) | 132 |

Symmetry code: (i) −x + 1, y + 1, −z + ½.

| Table 4 | Hydrogen-bond geometry (Å, °) for (IV). |
| D—H···A | D—H | H···A | D····A | D—H···A |
| N1—H1N···O1 | 0.88 (2) | 2.00 (2) | 2.8628 (18) | 164.9 (18) |
| C3—H3···N1’ | 0.95 | 2.78 | 3.718 (7) | 172 |
| C5—H5B···O1’ | 0.99 | 2.64 | 3.307 (2) | 125 |
| C7—H7···S1B | 0.95 | 2.65 | 3.534 (16) | 155 |
| C12—H12···S1B’ | 0.95 | 2.98 | 3.6624 (19) | 129 |

Symmetry codes: (i) −x + 1, y + ½, z − ½; (ii) x, −y + ½, z − ½; (iii) −x + 1, −y + 2, −z + 1.

H···Np (p = pyridine) hydrogen bonds: in the former, these links generate [001] C(7) chains (Fig. 5), with adjacent molecules in the chain related by the 21 screw axis. In (II), the equivalent interaction also leads to [001] chains (Fig. 6) generated by the 21 screw axis but here the graph-set motif is C(6). The packing for (IV) features classical C(4) amide N—H···O hydrogen bonds (Fig. 7) leading to [010] chains generated once again by a 21 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···Np link arising from the N-methyl group. The structures of (I), (II) and (IV) also feature various C—H···X (X = N, O, S) interactions although these are presumably very weak, given their H···X lengths.

The shortest aromatic ring centroid–centroid separations in these structures are $\pi_C \cdot \cdot \cdot \pi_C$ (I thiophene, p = pyridine) = 4.046 (2) Å (slippage = 1.546 Å) for (I), $\pi_C \cdot \cdot \cdot \pi_C$ = 4.0509 (12) Å (slippage = 1.929 Å) for (II), $\pi_C \cdot \cdot \cdot \pi_C$ = 4.7831 (9) Å for (III) and $\pi_C \cdot \cdot \cdot \pi_C$ = 4.643 (2) Å for (IV).
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···H (van der Waals) contacts the most significant for each structure, followed by C···H/H···C. The O···H/H···O and N···H/H···N contributions are almost the same for the four structures, despite the lack of classical hydrogen bonds in (III). The S···H/H···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···S close contact arising from the pyridine ring in the latter structures. It is notable that the percentage of O···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.

Table 5

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

Note: (a) Major disorder component.

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 6

Fragment of the crystal structure of (II) showing part of an [001] C(6) chain linked by N···H···N hydrogen bonds (double-dashed lines). Symmetry code: (i) 1 − x, 1 − y, z + 1/2.

Figure 7

Fragment of the crystal structure of (IV) showing part of an [010] C(4) chain linked by N···H···O hydrogen bonds (double-dashed lines). Symmetry codes: (i) 1 − x, 1/2 + y, 1/2 − z; (ii) 1 − x, y − 1/2, 1/2 − z.
Table 6
Experimental details.

|                  | (I)             | (II)            | (III)           | (IV)            |
|------------------|-----------------|-----------------|-----------------|-----------------|
| Chemical formula | C₁₁H₉N₃OS       | C₁₁H₉N₃OS       | C₁₁H₉N₃OS       | C₁₁H₉N₃OS       |
| M₁               | 231.27          | 231.27          | 245.30          | 245.30          |
| Crystal system, space group | Orthorhombic, Pca2₁ | Orthorhombic, Pna2₁ | Monoclinic, C2/c | Monoclinic, P2₁/c |
| Temperature (K)  | 100             | 100             | 100             | 100             |
| a, b, c (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) | 90, 95.265 (2), 90 |
| α, β, γ (°)      | 90, 90, 90      | 90, 90, 90      | 90, 95.265 (2), 90, 90, 95.265 (2), 90 | 8, 4, 8 |
| V (Å³)           | 1024.05 (16)    | 1057.19 (13)    | 2267.1 (3)      | 1152.27 (14)    |
| Z                | 4               | 4               | 8               | 4               |
| Radiation type   | Mo Kα           | Mo Kα           | Mo Kα           | Mo Kα           |
| 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 | 0.10 × 0.12 × 0.03 | 0.10 × 0.09 × 0.06 |
| Data collection  | Rigaku Saturn724+ CCD | Rigaku Saturn724+ CCD | Rigaku Saturn724+ CCD | Rigaku AFC12 CCD |
| Absorption correction | Multi-scan (CrystalClear; Rigaku, 2012) | Multi-scan (CrystalClear; Rigaku, 2012) | Multi-scan (CrystalClear; Rigaku, 2012) | Multi-scan (CrystalClear; Rigaku, 2012) |
| Tmin, Tmax       | 0.484, 1.000    | 0.756, 1.000    | 0.780, 1.000    | 0.723, 1.000    |
| No. of measured, independent and observed | 6740, 1822, 1559 | 7314, 1979, 1930 | 8717, 2563, 2307 | 8155, 2593, 2138 |
| reflections      | Rmerge, Rs value | 0.058, 0.026    | 0.022           | 0.031           |
| (sin θ/λ)max (Å⁻¹) | 0.649           | 0.649           | 0.650           | 0.670           |
| Refinement       | R[F² > 2σ(F²)], wR(F²), S | 0.046, 0.112, 1.08 | 0.029, 0.083, 1.08 | 0.031, 0.087, 1.07 |
| 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 |
| Δρmax, Δρmin (e Å⁻³) | 0.27, –0.43     | 0.33, –0.24     | 0.33, –0.29     | 0.32, –0.30     |
| Absolute structure | Parsons et al. (2013) | Parsons et al. (2013) | –              | –              |
| Absolute structure parameter | 0.02 (13)       | 0.04 (14)       | –              | –              |

Computers programs: CrystalClear (Rigaku, 2012), SHELXS97 (Sheldrick, 2008), SHELXL2018/3 (Sheldrick, 2015), ORTEP-3 for Windows (Farrugia, 2012) and pubICIF (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 Uiso 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 Uiso(H) = 1.2Ueq(N). All C-bound H atoms were located geometrically (C—H = 0.95–0.99 Å) and refined as riding atoms with Uiso(H) = 1.2Ueq(C) or 1.5Ueq(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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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_{9}N_{3}O_{2}S
Mr = 231.27
Orthorhombic, Pca \(_2\) \(_1\)
\(a = 10.6845\) (9) Å
\(b = 9.4974\) (9) Å
\(c = 10.0917\) (10) Å
\(V = 1024.05\) (16) Å\(^3\)
\(Z = 4\)
\(F(000) = 480\)

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

Refinement
Refinement on \(F^2\)
Least-squares matrix: full
\(R[F^2 > 2\sigma(F^2)] = 0.046\)
\(wR(F^2) = 0.112\)
\(S = 1.08\)
1822 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
\(w = 1/[\sigma(F_c^2) + (0.0492P)^2 + 0.5837P]\)
where \(P = (F_c^2 + 2F_{o}^2)/3\)
\((\Delta\sigma)_{\text{max}} < 0.001\)
\(\Delta\rho_{\text{max}} = 0.27\) e Å\(^{-3}\)
\(\Delta\rho_{\text{min}} = -0.43\) e Å\(^{-3}\)

Absolute structure: Parsons et al. (2013)
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 (Å²) |
|---|---|---|---|---|
| **x** | **y** | **z** | **U_{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) |
| C11 0.091113 | −0.306383 | 0.473419 | 0.027* |
| C12 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 (Å²)**

| C1 | C2 | C3 | C4 | C5 | C6 | H6 | C7 | C8 | H8 | C9 | H9 | C10 | C11 | H11 | N1 | H1N | N2 | N3 | O1 | S1 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| U11 | 0.030 (2) | 0.030 (2) | 0.026 (2) | 0.025 (2) | 0.026 (2) | 0.022 (2) | 0.024 (2) | 0.026 (2) | 0.022 (2) | 0.020 (2) | 0.025 (2) | 0.026 (2) | 0.025 (2) | 0.020 (2) | 0.019 (2) | 0.026 (2) | 0.020 (2) | 0.020 (2) | 0.025 (2) | 0.027 (2) | 0.023 (2) | 0.021 (2) |
| U22 | 0.022 (3) | 0.016 (3) | 0.022 (3) | 0.015 (2) | 0.016 (3) | 0.022 (3) | 0.024 (2) | 0.019 (2) | 0.017 (2) | 0.019 (2) | 0.017 (2) | 0.020 (2) | 0.017 (2) | 0.024 (2) | 0.017 (2) | 0.020 (2) | 0.019 (2) | 0.026 (2) | 0.017 (2) | 0.002 (2) | 0.006 (2) | 0.002 (2) |
| U33 | −0.0009 (18) | 0.0038 (18) | 0.0033 (16) | 0.0014 (16) | 0.0014 (16) | 0.002 (2) | 0.0014 (16) | 0.0002 (17) | −0.0002 (17) | −0.0012 (18) | −0.0014 (15) | 0.00001 (18) | −0.0014 (15) | 0.00001 (18) | −0.0006 (13) | −0.0002 (17) | 0.00001 (18) | −0.0002 (17) | 0.00001 (18) | 0.00001 (18) | 0.00001 (18) | 0.00001 (18) |
| U12 | −0.0001 (18) | 0.0000 (2) | −0.0001 (18) | −0.0002 (16) | −0.0002 (16) | 0.0001 (2) | −0.0001 (18) | 0.0002 (2) | 0.0002 (2) | 0.0016 (18) | 0.0001 (2) | 0.0002 (2) | 0.0001 (2) | 0.0002 (2) | 0.0001 (2) | 0.0001 (2) | 0.0001 (2) | 0.0001 (2) | 0.0001 (2) | 0.0001 (2) | 0.0001 (2) | 0.0001 (2) |
| U13 | 0.009 (2) | 0.000 (2) | 0.0004 (18) | 0.001 (18) | 0.0016 (18) | 0.000 (2) | 0.0016 (18) | 0.001 (18) | 0.001 (18) | 0.001 (18) | 0.001 (18) | 0.001 (18) | 0.001 (18) | 0.001 (18) | 0.001 (18) | 0.001 (18) | 0.001 (18) | 0.001 (18) | 0.001 (18) | 0.001 (18) | 0.001 (18) | 0.001 (18) |
| U23 | 0.0002 (2) | 0.0000 (2) | 0.0000 (2) | 0.0002 (2) | 0.0002 (2) | 0.0000 (2) | 0.0000 (2) | 0.0002 (2) | 0.0002 (2) | 0.0002 (2) | 0.0002 (2) | 0.0002 (2) | 0.0002 (2) | 0.0002 (2) | 0.0002 (2) | 0.0002 (2) | 0.0002 (2) | 0.0002 (2) | 0.0002 (2) | 0.0002 (2) | 0.0002 (2) | 0.0002 (2) | 0.0002 (2) |

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supporting information

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, °)

| Bond/Angle | Distance/Angle | Distance/Angle |
|------------|----------------|----------------|
| 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)        |
| 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)         |

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Hydrogen-bond geometry (Å, °)

| D—H···A  | D—H  | H···A  | D···A  | D—H···A |
|----------|-------|--------|--------|---------|
| N1—H1N···N3i | 0.87 (5) | 2.14 (5) | 2.995 (5) | 166 (4) |
| C1—H1···O1ii | 0.95 | 2.53 | 3.471 (6) | 171 |
| C3—H3···N3i | 0.95 | 2.61 | 3.479 (6) | 152 |
| C6—H6···N3i | 0.95 | 2.59 | 3.410 (6) | 145 |
| C9—H9···O1iii | 0.95 | 2.66 | 3.397 (5) | 135 |
| C11—H11···N2iv | 0.95 | 2.57 | 3.481 (6) | 160 |

Symmetry codes: (i) −x, −y, −z−1/2; (ii) −x+1, −y, −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 | Ds = 1.453 Mg m−3 |
| Orthorhombic, Pna21 | Mo Kα radiation, λ = 0.71073 Å |
| a = 18.4056 (13) Å | Cell parameters from 6000 reflections |
| b = 9.5255 (7) Å | θ = 2.4–27.5° |
| c = 6.0300 (4) Å | μ = 0.29 mm−1 |
| V = 1057.19 (13) Å³ | T = 100 K |
| Z = 4 | Blade, dark orange |
| F(000) = 480 | 0.15 x 0.06 x 0.04 mm |

Data collection

| Rigaku Saturn724+ CCD | 1979 independent reflections |
| diffractometer | 1930 reflections with I > 2σ(I) |
| ω scans | Rint = 0.026 |
| Absorption correction: multi-scan | θmax = 27.5°, θmin = 3.1° |
| (CrystalClear; Rigaku, 2012) | h = −23→23 |
| Tmin = 0.756, Tmax = 1.000 | k = −9→12 |
| 7314 measured reflections | l = −5→7 |

Refinement

| Refinement on F² | Primary atom site location: structure-invariant direct methods |
| Least-squares matrix: full | Hydrogen site location: mixed |
| R(F² > 2σ(F²)) = 0.029 | H atoms treated by a mixture of independent and constrained refinement |
| wR(F²) = 0.083 | w = 1/[σ²(Fo²) + (0.0573P)² + 0.2224P] |
| S = 1.08 | where P = (Fo² + 2Fo²)/3 |
| 1979 reflections | (Δ/σ)max = 0.001 |
| 148 parameters | |
| 1 restraint | |

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Δρ_{max} = 0.33 e Å^{-3}
Δρ_{min} = -0.24 e Å^{-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 (Å²)

|   | x         | y         | z         | U_{iso}*/U_{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 (Å²)

|   | 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) 0.0284 (9) 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, °)

| Bond/Angle | Distance/Angle (Å, °) |
|------------|----------------------|
| C1—C2      | 1.365 (4)            |
| C1—S1      | 1.702 (2)            |
| C1—H1      | 0.9500               |
| C2—C3      | 1.434 (3)            |
| C2—H2      | 0.9500               |
| C3—C4      | 1.415 (3)            |
| C3—H3      | 0.9500               |
| C4—C5      | 1.485 (3)            |
| C4—S1      | 1.728 (2)            |
| C5—C6      | 1.232 (3)            |
| C5—N2      | 1.361 (3)            |
| C6—N3      | 1.361 (3)            |
| C6—C7      | 1.284 (3)            |
| C6—C7      | 1.463 (3)            |
| C1—C2—C3  | 109.9 (2)            |
| C1—C2—H2  | 123.3                |
| C2—C3—C4  | 121.3 (2)            |
| C2—C3—H3  | 125.1                |
| C3—C4—C5  | 112.16 (16)          |
| C5—C4—S1  | 112.16 (16)          |
| C5—C4—C1  | 126.50 (18)          |
| C5—C4—C3  | 119.15 (19)          |
| C5—C4—C4  | 120.7 (2)            |
| C5—C4—C5  | 120.1 (2)            |
| C2—C1—C3  | 113.11 (17)          |
| C2—C1—H1  | 123.4                |
| C1—C2—C3  | 113.4 (2)            |
| C1—C2—H2  | 123.3                |
| C2—C3—H3  | 125.1                |
| C3—C4—C5  | 112.16 (16)          |
| C5—C4—S1  | 112.16 (16)          |
| C5—C4—C1  | 126.50 (18)          |
| C5—C4—C3  | 119.15 (19)          |
| C5—C4—C4  | 120.7 (2)            |
| C5—C4—C5  | 120.1 (2)            |
| C2—C1—C3  | 113.11 (17)          |
| C2—C1—H1  | 123.4                |
| C1—C2—C3  | 113.4 (2)            |
| C1—C2—H2  | 123.3                |
| C2—C3—H3  | 125.1                |
| C3—C4—C5  | 112.16 (16)          |
| C5—C4—S1  | 112.16 (16)          |
| C5—C4—C1  | 126.50 (18)          |
| C5—C4—C3  | 119.15 (19)          |
| C5—C4—C4  | 120.7 (2)            |
| C5—C4—C5  | 120.1 (2)            |
| C2—C1—C3  | 113.11 (17)          |
| C2—C1—H1  | 123.4                |
| C1—C2—C3  | 113.4 (2)            |
| C1—C2—H2  | 123.3                |
| C2—C3—H3  | 125.1                |
| C3—C4—C5  | 112.16 (16)          |
| C5—C4—S1  | 112.16 (16)          |
| C5—C4—C1  | 126.50 (18)          |
| C5—C4—C3  | 119.15 (19)          |
| C5—C4—C4  | 120.7 (2)            |
| C5—C4—C5  | 120.1 (2)            |

**Notes:**
- All distances and angles are given in Å and °, respectively.
- All values are reported with their standard deviations in parentheses.
- Distances are typical bond lengths, while angles represent the geometric arrangement of atoms.

**References:**
- Acta Cryst. (2022). E78, 619-624
- sup-6
C2—C3—C4—C5 −176.80 (19) 
C2—C3—C4—S1 0.2 (2) 
C3—C4—C5—O1 5.8 (3) 
C3—C4—C5—N1 −176.02 (19) 
S1—C4—C5—O1 −170.67 (17) 
C3—C4—C5—N1 −176.80 (19) 
C3—C4—C5—O1 5.8 (3) 
S1—C4—C5—O1 −170.67 (17) 
C2—C1—S1—C4 1.60 (19) 
N3—C7—C8—C9 1.8 (4) 
C6—C7—C8—C9 −178.0 (2) 
C7—C8—C9—C10 0.8 (4) 

Hydrogen-bond geometry (Å, °)

| D—H···A | D—H | H···A | D···A | D—H···A |
|---------|------|-------|-------|---------|
| N1—H1N···N3i | 0.98 (3) | 2.03 (3) | 3.013 (3) | 177 (3) |
| C1—H1···O1ii | 0.95 | 2.48 | 3.101 (3) | 123 |
| C2—H2···O1iii | 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

Mr = 245.30

Monoclinic, C2/c

a = 21.0690 (15) Å
b = 5.1085 (4) Å

θ = 2.9–27.5°

Mo Kα radiation, λ = 0.71073 Å

Cell parameters from 7400 reflections

θ = 2.9–27.5°

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)

Tmin = 0.780, Tmax = 1.000

2307 reflections with I > 2σ(I)

2563 independent reflections

2307 reflections with I > 2σ(I)

Refinement

Refinement on F2

Least-squares matrix: full

R[F2 > 2σ(F2)] = 0.031

wR(F2) = 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(F2) + (0.0408P)2 + 2.1991P]

where P = (F2 + 2F2)/3

(Δ/σ)max = 0.001

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

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

**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 (Å²)**

|    | x      | y      | z      | $U_{\text{iso}}$ / $U_{\text{eq}}$ |
|----|--------|--------|--------|-----------------------------------|
| 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* |
| C7 | 0.262463 | 0.059115 | 0.359010 | 0.034* |
| H7 | 0.32615 (6) | 0.1249 (3) | 0.25363 (6) | 0.0190 (3) |
| C8 | 0.298098 | -0.007769 | 0.265792 | 0.023* |
| C9 | 0.33189 (6) | 0.1729 (2) | 0.18583 (6) | 0.0178 (3) |
| C10 | 0.36845 (6) | 0.3762 (3) | 0.16384 (6) | 0.0197 (3) |
| C11 | 0.392055 | 0.489970 | 0.192720 | 0.024* |
| C12 | 0.36941 (6) | 0.4078 (3) | 0.09876 (6) | 0.0222 (3) |
| H12 | 0.393440 | 0.545017 | 0.082220 | 0.027* |
| C13 | 0.33481 (7) | 0.2364 (3) | 0.05837 (6) | 0.0247 (3) |
| H13 | 0.334717 | 0.253470 | 0.013642 | 0.030* |
| C14 | 0.30036 (7) | 0.0398 (3) | 0.08438 (6) | 0.0266 (3) |
| H14 | 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 (Å²)**

|    | $U_1^{11}$ | $U_1^{22}$ | $U_1^{33}$ | $U_1^{12}$ | $U_1^{13}$ | $U_1^{23}$ |
|----|------------|------------|------------|------------|------------|------------|
| 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) |

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Geometric parameters (Å, °)

| Bond                  | Distance (Å) | Angle (°)   |
|-----------------------|--------------|-------------|
| C1—C2                 | 1.359 (2)    |             |
| C1—S1                 | 1.7075 (14)  |             |
| C1—H1                 | 0.9500       |             |
| C2—C3                 | 1.414 (2)    |             |
| C2—H2                 | 0.9500       |             |
| C3—C4                 | 1.3894 (19)  |             |
| C3—H3                 | 0.9500       |             |
| C4—C5                 | 1.4817 (19)  |             |
| C4—S1                 | 1.7223 (13)  |             |
| C5—O1                 | 1.2225 (16)  |             |
| C5—N1                 | 1.3780 (17)  |             |
| C6—N1                 | 1.4545 (17)  |             |
| C6—H6A                | 0.9800       |             |
| C6—H6B                | 0.9800       |             |
| C6—H6C                | 0.9800       |             |
| C2—C1—S1              | 112.41 (11)  |             |
| C2—C1—H1              | 123.8        |             |
| S1—C1—H1              | 123.8        |             |
| C1—C2—C3              | 112.48 (13)  |             |
| C1—C2—H2              | 123.8        |             |
| C3—C2—H2              | 123.8        |             |
| C4—C3—C2              | 112.53 (12)  |             |
| C4—C3—H3              | 123.7        |             |
| C2—C3—H3              | 123.7        |             |
| C3—C4—C5              | 120.19 (12)  |             |
| C3—C4—S1              | 110.61 (10)  |             |
| C5—C4—S1              | 129.19 (10)  |             |
| O1—C5—N1              | 120.00 (13)  |             |
| O1—C5—C4              | 119.42 (12)  |             |
| N1—C5—C4              | 120.58 (11)  |             |
| N1—C6—H6A             | 109.5        |             |
| N1—C6—H6B             | 109.5        |             |
| H6A—C6—H6B            | 109.5        |             |
N1—C6—H6C 109.5  
H6A—C6—H6C 109.5  
H6B—C6—H6C 109.5  
N2—C7—C8 121.06 (12)  
N2—C7—H7 119.5  
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—C4—C5—O1 178.88 (10)  
N2—C7—C8—N3 176.35 (12)  
C1—S1—C4—C5 0.04 (15)  
N2—C7—C8—C9 −4.8 (2)  
C2—C3—C4—C5 −179.06 (12)  
C3—C4—C5—N1 121.06 (12)  
C1—S1—C4—C5 −1.69 (19)  
C2—C3—C4—S1 0.02 (18)  
C3—C4—C5—O1 −2.21 (19)  
C4—C5—N1—N2 −1.19 (18)  
S1—C4—C5—O1 −0.08 (16)  
C4—C5—N1—C6 −178.37 (11)  
S1—C4—C5—N1 −1.69 (19)  
C5—N1—N2—C7 179.40 (12)  
N2—C7—C8—N3 176.35 (12)  
C7—N2—N1−C6 119.89 (11)  
C8—C7—N2—N1 −3.49 (18)  
N2—C7—C8—C9 −4.8 (2)  
C7—C8—N3—C12 179.38 (12)  
C8—C7—N2—N1 −179.79 (11)  
N3—C8—C9—C10 0.3 (2)  
C7—C8—N3—C12 179.38 (12)  
N2—C7—C8—C9 −4.8 (2)  
C9—C8—N3—C12 0.5 (2)  
N3—C8—C9—C10 0.3 (2)  
C8—C7—N2—N1 −179.79 (11)  
C7—C8—C9—C10 −178.51 (12)  
N2—C7—C8—N3 176.35 (12)  
C8—C7—N2—N1 −179.79 (11)  
C8—C7—C8−C9 176.35 (12)  
C7—C8—C9—C10 −178.51 (12)  
C9—C10—C11—C12 0.1 (2)  
N2—C7—C8—C9 −4.8 (2)  
C11—C12—N3—C8 0.7 (2)  
C10—C11—C12—N3 0.7 (2)  
C9—C10—C11—C12 0.1 (2)  
C12—N3—C8—C9 176.35 (12)  
C7—C8—C9—C10 −178.51 (12)  
C9—C10—C11—C12 0.1 (2)  
C7—C8—C9—C10 −178.51 (12)  
C8—C7—C8—C9 −178.51 (12)  
N2—C7—C8—N3 176.35 (12)  
C11—C12—N3—C8 0.7 (2)  
Hydrogen-bond geometry (Å, °)

| D—H···A | D—H  | H···A | D···A   | D—H···A |
|---------|------|------|--------|--------|
| C9—H9···S1 | 0.95 | 2.84 | 3.7217 (13) | 155 |
| C6—H6C···N3i | 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

C12H11N3OS  
F(000) = 512  
M_r = 245.30  
D_x = 1.414 Mg m^−3  
Monoclinic, P2_1/c  
Cell parameters from 43879 reflections  
a = 11.3963 (8) Å  
b = 9.2782 (7) Å  
c = 11.8178 (8) Å  
θ = 2.9–27.5°  
μ = 0.27 mm^−1  
β = 112.761 (2)°  
T = 100 K  
V = 1152.27 (14) Å^3  
Z = 4  

Data collection

Rigaku AFC12 CCD  
2593 independent reflections  
diffractometer  
2138 reflections with l > 2σ(l)  
ω scans  
R_m = 0.031  
Absorption correction: multi-scan  
CrystalClear; Rigaku, 2012  
θ_max = 28.4°, θ_min = 2.9°  
h = −15→14  
T_min = 0.723, T_max = 1.000  
k = −12→11  
l = −14→14  
8155 measured reflections  

### 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

$w = 1/[\sigma^2(F_o^2) + (0.0505P)^2 + 0.7045P]$

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

$\Delta\rho_{\text{max}} = 0.32 \, \text{e} \, \text{Å}^{-3}$

$\Delta\rho_{\text{min}} = -0.30 \, \text{e} \, \text{Å}^{-3}$

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**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 ($\AA^2$)**

| Atom  | $x$     | $y$     | $z$     | $U_{eq}$/$U_{iso}$ | Occ. (<1) |
|-------|---------|---------|---------|--------------------|-----------|
| C1    | 0.9466  | 0.7136  | 0.2749  | 0.0222 (5)         | 0.851 (2) |
| H1    | 1.033688| 0.689483| 0.317920| 0.027*             | 0.851 (2) |
| C2    | 0.8750  | 0.6617  | 0.1571  | 0.0203 (5)         | 0.851 (2) |
| H2    | 0.905946| 0.598307| 0.111806| 0.024*             | 0.851 (2) |
| C3    | 0.7527  | 0.7158  | 0.1161  | 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    | 0.60108 (15)| 0.86577 (18) | 0.19459 (16) | 0.0231 (3) | 0.149 (2) |
| 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*         |           |
### Atomic displacement parameters (Å²)

| Atom | $U^{11}$  | $U^{22}$  | $U^{33}$  | $U^{12}$  | $U^{13}$  | $U^{23}$  |
|------|-----------|-----------|-----------|-----------|-----------|-----------|
| 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  | 0.0146 (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   | 0.0274 (7) | 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, °)

| Bond     | Distance  | Angle       |
|----------|-----------|-------------|
| C1—C2   | 1.399 (3) | 1.399 (16)  |
| C1—S1   | 1.716 (2) | C5—H5A 0.9900 |
| C1—H1   | 0.9500    | C5—H5B 0.9900 |
| C2—C3   | 1.380 (8) | C6—O1 1.222 (2) |
| C2—H2   | 0.9500    | C6—N1 1.362 (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) |
| Bond | Distance (Å) | Bond | Distance (Å) |
|------|-------------|------|-------------|
| 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 | 115.03 (15) |
| C3—C4—S1 | 112.4 (3) | C9—C8—C7 | 122.07 (15) |
| C5—C4—S1 | 119.63 (13) | C10—C9—C8 | 119.07 (16) |
| C1—S1—C4 | 89.14 (10) | C10—C9—H9 | 120.5 |
| 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 |

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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) C5—C6—N1—N2 179.18 (13)
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, °)

| D—H—A          | D—H  | H···A  | D···A    | D—H···A  |
|-----------------|-------|--------|----------|----------|
| N1—H1N···O1i    | 0.88 (2) | 2.00 (2) | 2.8628 (18) | 164.9 (18) |
| C3—H3···N1i     | 0.95   | 2.78   | 3.718 (7) | 172      |
| C5—H5B···O1i    | 0.99   | 2.64   | 3.307 (2) | 125      |
| C7—H7···S1B     | 0.95   | 2.65   | 3.534 (16) | 155      |
| C12—H12···S1iii | 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.