

N-(5-Ethylsulfanyl-1,3,4-thiadiazol-2-yl)-2-(4,5,6,7-tetrahydrothieno[3,2-c]pyridin-5-yl)acetamide

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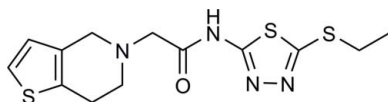
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Key indicators: single-crystal X-ray study; $T = 113$ K; mean $\sigma(\text{C}-\text{C}) = 0.002$ Å; R factor = 0.030; wR factor = 0.079; data-to-parameter ratio = 18.2.

In the title compound, $\text{C}_{13}\text{H}_{16}\text{N}_4\text{OS}_3$, a thienopyridine-derivative, the tetrahydropyridine ring exhibits a half-chair conformation, and the folded conformation of the molecule is defined by the $\text{N}-\text{C}-\text{C}-\text{N}$ torsion angle of -78.85 (16)°. The crystal packing features intermolecular $\text{C}-\text{H}\cdots\text{N}$, $\text{N}-\text{H}\cdots\text{N}$ and $\text{C}-\text{H}\cdots\text{O}$ hydrogen bonds.

Related literature

The title compound is a potential antiplatelet agent. As irreversible P2Y12 antagonists, thienopyridines have proved the relevance of inhibiting signaling *via* the platelet-specific P2Y12 ADP receptor in the prevention of cardiovascular events, see: Iyengar (2009); Franchini & Mannucci, (2009); Van Giezen *et al.* (2009); Van Giezen & Humphries (2005). For a related structure, see: Chen *et al.* (2010). For the synthesis of the title compound, see: Liu *et al.* (2008).



Experimental

Crystal data

$\text{C}_{13}\text{H}_{16}\text{N}_4\text{OS}_3$

$M_r = 340.48$

Monoclinic, $P2_1/n$

$a = 6.532$ (4) Å

$b = 9.788$ (6) Å

$c = 23.491$ (15) Å

$\beta = 95.524$ (6)°

$V = 1494.8$ (16) Å³

$Z = 4$

Mo $K\alpha$ radiation

$\mu = 0.50$ mm⁻¹

$T = 113$ K

$0.28 \times 0.22 \times 0.18$ mm

Data collection

Rigaku Saturn CCD area-detector diffractometer

Absorption correction: multi-scan (*CrystalClear*; Rigaku/MS, 2005)

$T_{\min} = 0.873$, $T_{\max} = 0.916$

12423 measured reflections

3545 independent reflections

2653 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.036$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.030$

$wR(F^2) = 0.079$

$S = 1.03$

3545 reflections

195 parameters

1 restraint

H atoms treated by a mixture of independent and constrained refinement

$\Delta\rho_{\text{max}} = 0.44$ e Å⁻³

$\Delta\rho_{\text{min}} = -0.23$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|--|----------|-------------|-------------|---------------|
| $\text{C12}-\text{H12B}\cdots\text{N1}^i$ | 0.99 | 2.60 | 3.473 (3) | 147 |
| $\text{N2}-\text{H2}\cdots\text{N3}^{ii}$ | 0.89 (1) | 2.02 (1) | 2.902 (2) | 171 (2) |
| $\text{C5}-\text{H5}\cdots\text{O1}^{iii}$ | 0.95 | 2.46 | 3.279 (2) | 145 |

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

Data collection: *CrystalClear* (Rigaku/MS, 2005); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *CrystalStructure* (Rigaku/MS, 2005).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: KP2327).

References

- Chen, J.-F., Liu, Y., Wang, J.-Y. & Liu, D.-K. (2010). *Acta Cryst.* E66, o3213.
- Franchini, M. & Mannucci, P. M. (2009). *Eur. J. Int. Med.* **20**, 733–738.
- Iyengar, S. (2009). *J. Thromb. Thrombolysis*, **27**, 300–306.
- Liu, D. K., Liu, Y., Liu, M., Zhang, S. J., Cheng, D., Jin, L. Y., Xu, W. R. & Liu, C. X. (2008). CN Patent 101284838A.
- Rigaku/MS (2005). *CrystalClear* and *CrystalStructure*. Rigaku/MS Inc., The Woodlands, Texas, USA.
- Sheldrick, G. M. (2008). *Acta Cryst.* A64, 112–122.
- Van Giezen, J. J. J., Berntsson, P., Zachrisson, H. & Bjorkman, J. A. (2009). *Thromb. Res.* **124**, 565–571.
- Van Giezen, J. J. J. & Humphries, R. G. (2005). *Sem. Thromb. Hemost.* **31**, 195–204.

supplementary materials

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N-(5-Ethylsulfanyl-1,3,4-thiadiazol-2-yl)-2-(4,5,6,7-tetrahydrothieno[3,2-*c*]pyridin-5-yl)acetamide

S. Zhi, S. Mu, Y. Liu and D.-K. Liu

Comment

As irreversible P2Y₁₂ antagonists, the thienopyridines (*e.g.*, clopidogrel and prasugrel) have been further proved the relevance of inhibiting signaling *via* the platelet-specific P2Y₁₂ ADP receptor in the prevention of cardiovascular events (Iyengar, 2009; Van Giezen & Humphries, 2005; Franchini, *et al.*, 2009). The structure of the title compound (I), a new derivative of thienopyridine, is presented here.

The tetrahydropyridine ring is in a half-chair conformation (Fig. 1). The thiadiazole ring plane (r.m.s. deviation 0.0020 Å) and the acidamide plane (r.m.s. deviation 0.0074 Å) are almost coplanar, with a dihedral angle of 3.24 (9)°. The dihedral angles formed between the thiadiazole ring plane and the thiophene ring plane, the acidamide plane and the thiophene ring plane are 76.19 (6)° and 78.47 (7)°, respectively. Crystal packing is via hydrogen bonds C—H⋯N, N—H⋯N and C—H⋯O (Table 1, Fig. 2).

Experimental

Chloroacetyl chloride was dropwisely added into a mixture of 5-(ethylthio)-1,3,4-thiadiazol-2-amine, TEA and DMF at 268 K. After stirred for 3 h, the mixture was poured into cold water. 2-Chloro-*N*-(5-(ethylthio)-1,3,4-thiadiazol-2-yl)acetamide was precipitated as an intermediate. Then the intermediate, equimolar quantities thienopyridine salt and TEA were refluxed for 5 h in acetonitrile, and the product was obtained by silica gel column chromatography. Crystallisation of the obtained yellow solid from methanol afforded light-yellow crystals suitable for X-ray analysis.

Refinement

The N—H bond was restrained to 0.90 Å, and other H atoms were positioned geometrically and refined using a riding model, with $d(\text{C—H})=0.95\text{--}0.99$ Å, and $U_{\text{iso}}(\text{H})=1.2U_{\text{eq}}(\text{C})$ of the parent atom.

Figures

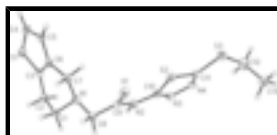


Fig. 1. The molecular structure of (I), with the atom-numbering scheme and 50% probability displacement ellipsoids.

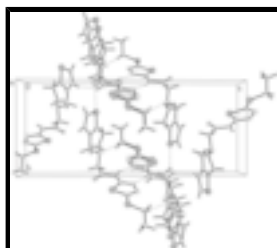


Fig. 2. Packing diagram for (I) with hydrogen bonds drawn as dashed lines.

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N-(5-Ethylsulfanyl-1,3,4-thiadiazol-2-yl)-2-(4,5,6,7-tetrahydrothieno[3,2-*c*]pyridin-5-yl)acetamide

Crystal data

| | |
|---------------------------------|---|
| $C_{13}H_{16}N_4OS_3$ | $F(000) = 712$ |
| $M_r = 340.48$ | $D_x = 1.513 \text{ Mg m}^{-3}$ |
| Monoclinic, $P2_1/n$ | Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$ |
| Hall symbol: -P 2yn | Cell parameters from 4582 reflections |
| $a = 6.532 (4) \text{ \AA}$ | $\theta = 1.7\text{--}27.9^\circ$ |
| $b = 9.788 (6) \text{ \AA}$ | $\mu = 0.50 \text{ mm}^{-1}$ |
| $c = 23.491 (15) \text{ \AA}$ | $T = 113 \text{ K}$ |
| $\beta = 95.524 (6)^\circ$ | Prism, colourless |
| $V = 1494.8 (16) \text{ \AA}^3$ | $0.28 \times 0.22 \times 0.18 \text{ mm}$ |
| $Z = 4$ | |

Data collection

| | |
|---|--|
| Rigaku Saturn CCD area-detector diffractometer | 3545 independent reflections |
| Radiation source: rotating anode multilayer | 2653 reflections with $I > 2\sigma(I)$ |
| Detector resolution: $14.63 \text{ pixels mm}^{-1}$ | $R_{\text{int}} = 0.036$ |
| ω and φ scans | $\theta_{\text{max}} = 27.9^\circ$, $\theta_{\text{min}} = 1.7^\circ$ |
| Absorption correction: multi-scan (<i>CrystalClear</i> ; Rigaku/MSO, 2005) | $h = -8 \rightarrow 8$ |
| $T_{\text{min}} = 0.873$, $T_{\text{max}} = 0.916$ | $k = -12 \rightarrow 12$ |
| 12423 measured reflections | $l = -28 \rightarrow 30$ |

Refinement

| | |
|---------------------------------|--|
| Refinement on F^2 | Primary atom site location: structure-invariant direct methods |
| Least-squares matrix: full | Secondary atom site location: difference Fourier map |
| $R[F^2 > 2\sigma(F^2)] = 0.030$ | Hydrogen site location: inferred from neighbouring sites |
| $wR(F^2) = 0.079$ | H atoms treated by a mixture of independent and constrained refinement |
| $S = 1.03$ | $w = 1/[\sigma^2(F_o^2) + (0.042P)^2]$ |
| 3545 reflections | where $P = (F_o^2 + 2F_c^2)/3$ |
| 195 parameters | $(\Delta/\sigma)_{\text{max}} = 0.004$ |
| 1 restraint | $\Delta\rho_{\text{max}} = 0.44 \text{ e \AA}^{-3}$ |
| | $\Delta\rho_{\text{min}} = -0.23 \text{ e \AA}^{-3}$ |

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations

between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

| | <i>x</i> | <i>y</i> | <i>z</i> | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|------|--------------|---------------|---------------|----------------------------------|
| S1 | 1.09432 (6) | -0.17109 (4) | 0.167990 (17) | 0.02366 (11) |
| S2 | 0.59937 (6) | 0.64557 (4) | 0.091056 (16) | 0.01921 (10) |
| S3 | 0.24260 (6) | 0.77190 (4) | 0.021966 (17) | 0.02324 (11) |
| O1 | 0.87853 (17) | 0.54420 (11) | 0.17006 (4) | 0.0257 (3) |
| N1 | 1.16286 (18) | 0.27779 (12) | 0.15327 (5) | 0.0188 (3) |
| N2 | 0.9587 (2) | 0.51028 (13) | 0.08012 (5) | 0.0195 (3) |
| N3 | 0.76496 (19) | 0.59529 (13) | -0.00107 (5) | 0.0199 (3) |
| N4 | 0.58266 (19) | 0.66332 (13) | -0.01858 (5) | 0.0196 (3) |
| C1 | 1.3598 (2) | 0.20466 (16) | 0.15877 (7) | 0.0220 (3) |
| H1A | 1.4181 | 0.2046 | 0.1993 | 0.026* |
| H1B | 1.4584 | 0.2513 | 0.1359 | 0.026* |
| C2 | 1.3270 (2) | 0.05905 (16) | 0.13799 (7) | 0.0233 (3) |
| H2A | 1.2955 | 0.0577 | 0.0959 | 0.028* |
| H2B | 1.4531 | 0.0045 | 0.1479 | 0.028* |
| C3 | 1.1520 (2) | 0.00006 (15) | 0.16615 (6) | 0.0194 (3) |
| C4 | 0.8868 (2) | -0.14081 (15) | 0.20530 (7) | 0.0234 (3) |
| H4 | 0.7989 | -0.2103 | 0.2173 | 0.028* |
| C5 | 0.8627 (2) | -0.00627 (15) | 0.21566 (6) | 0.0214 (3) |
| H5 | 0.7562 | 0.0299 | 0.2360 | 0.026* |
| C6 | 1.0153 (2) | 0.07498 (15) | 0.19257 (6) | 0.0184 (3) |
| C7 | 1.0281 (2) | 0.22806 (15) | 0.19494 (6) | 0.0197 (3) |
| H7A | 0.8889 | 0.2676 | 0.1865 | 0.024* |
| H7B | 1.0824 | 0.2573 | 0.2338 | 0.024* |
| C8 | 1.1928 (2) | 0.42478 (15) | 0.15876 (7) | 0.0220 (3) |
| H8A | 1.3052 | 0.4538 | 0.1361 | 0.026* |
| H8B | 1.2324 | 0.4484 | 0.1993 | 0.026* |
| C9 | 0.9969 (2) | 0.49862 (14) | 0.13783 (7) | 0.0204 (3) |
| C10 | 0.7907 (2) | 0.57771 (14) | 0.05403 (6) | 0.0181 (3) |
| C11 | 0.4826 (2) | 0.69389 (15) | 0.02453 (6) | 0.0190 (3) |
| C12 | 0.2098 (3) | 0.84165 (17) | -0.04979 (7) | 0.0300 (4) |
| H12A | 0.3070 | 0.7958 | -0.0734 | 0.036* |
| H12B | 0.0686 | 0.8216 | -0.0669 | 0.036* |
| C13 | 0.2449 (3) | 0.99201 (18) | -0.05141 (8) | 0.0362 (4) |
| H13A | 0.1524 | 1.0379 | -0.0271 | 0.054* |
| H13B | 0.2173 | 1.0249 | -0.0908 | 0.054* |
| H13C | 0.3879 | 1.0121 | -0.0374 | 0.054* |
| H2 | 1.047 (2) | 0.4714 (17) | 0.0587 (7) | 0.038 (5)* |

supplementary materials

Atomic displacement parameters (\AA^2)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|-----|-------------|--------------|-------------|--------------|--------------|---------------|
| S1 | 0.0286 (2) | 0.0204 (2) | 0.0220 (2) | 0.00424 (17) | 0.00251 (17) | 0.00018 (16) |
| S2 | 0.0206 (2) | 0.02023 (18) | 0.0177 (2) | 0.00016 (15) | 0.00653 (16) | -0.00083 (15) |
| S3 | 0.0217 (2) | 0.0242 (2) | 0.0244 (2) | 0.00316 (16) | 0.00550 (17) | 0.00097 (16) |
| O1 | 0.0338 (7) | 0.0255 (6) | 0.0190 (6) | 0.0047 (5) | 0.0095 (5) | 0.0034 (5) |
| N1 | 0.0177 (7) | 0.0200 (6) | 0.0189 (7) | 0.0010 (5) | 0.0038 (5) | 0.0011 (5) |
| N2 | 0.0192 (7) | 0.0222 (6) | 0.0178 (7) | 0.0017 (5) | 0.0052 (5) | -0.0018 (5) |
| N3 | 0.0185 (7) | 0.0228 (6) | 0.0186 (7) | -0.0007 (5) | 0.0030 (5) | -0.0029 (5) |
| N4 | 0.0179 (7) | 0.0210 (6) | 0.0200 (7) | -0.0015 (5) | 0.0026 (5) | -0.0019 (5) |
| C1 | 0.0165 (8) | 0.0283 (8) | 0.0213 (8) | 0.0002 (6) | 0.0017 (6) | -0.0002 (6) |
| C2 | 0.0190 (8) | 0.0286 (8) | 0.0224 (8) | 0.0039 (7) | 0.0031 (7) | -0.0024 (7) |
| C3 | 0.0197 (8) | 0.0213 (7) | 0.0164 (8) | 0.0025 (6) | -0.0016 (6) | 0.0005 (6) |
| C4 | 0.0278 (9) | 0.0243 (8) | 0.0181 (8) | -0.0009 (7) | 0.0020 (7) | 0.0045 (6) |
| C5 | 0.0235 (8) | 0.0252 (8) | 0.0157 (8) | 0.0019 (6) | 0.0031 (6) | 0.0020 (6) |
| C6 | 0.0198 (8) | 0.0210 (7) | 0.0141 (7) | 0.0014 (6) | -0.0003 (6) | 0.0012 (6) |
| C7 | 0.0198 (8) | 0.0223 (7) | 0.0174 (8) | 0.0003 (6) | 0.0042 (6) | -0.0009 (6) |
| C8 | 0.0216 (8) | 0.0220 (8) | 0.0223 (8) | -0.0037 (6) | 0.0020 (7) | 0.0002 (6) |
| C9 | 0.0248 (8) | 0.0154 (7) | 0.0216 (8) | -0.0056 (6) | 0.0049 (7) | 0.0010 (6) |
| C10 | 0.0191 (8) | 0.0166 (7) | 0.0195 (8) | -0.0025 (6) | 0.0067 (6) | -0.0013 (6) |
| C11 | 0.0193 (8) | 0.0176 (7) | 0.0200 (8) | -0.0034 (6) | 0.0024 (6) | -0.0011 (6) |
| C12 | 0.0335 (10) | 0.0342 (9) | 0.0216 (9) | 0.0088 (8) | -0.0004 (7) | -0.0013 (7) |
| C13 | 0.0387 (11) | 0.0375 (10) | 0.0303 (10) | -0.0098 (8) | -0.0067 (8) | 0.0095 (8) |

Geometric parameters (\AA , $^\circ$)

| | | | |
|--------|-------------|----------|-----------|
| S1—C4 | 1.7096 (18) | C2—H2A | 0.9900 |
| S1—C3 | 1.7186 (18) | C2—H2B | 0.9900 |
| S2—C10 | 1.7232 (16) | C3—C6 | 1.352 (2) |
| S2—C11 | 1.7372 (18) | C4—C5 | 1.351 (2) |
| S3—C11 | 1.7396 (18) | C4—H4 | 0.9500 |
| S3—C12 | 1.812 (2) | C5—C6 | 1.423 (2) |
| O1—C9 | 1.2179 (18) | C5—H5 | 0.9500 |
| N1—C8 | 1.456 (2) | C6—C7 | 1.501 (2) |
| N1—C7 | 1.4614 (18) | C7—H7A | 0.9900 |
| N1—C1 | 1.467 (2) | C7—H7B | 0.9900 |
| N2—C9 | 1.359 (2) | C8—C9 | 1.510 (2) |
| N2—C10 | 1.373 (2) | C8—H8A | 0.9900 |
| N2—H2 | 0.885 (9) | C8—H8B | 0.9900 |
| N3—C10 | 1.300 (2) | C12—C13 | 1.490 (3) |
| N3—N4 | 1.3914 (18) | C12—H12A | 0.9900 |
| N4—C11 | 1.2921 (19) | C12—H12B | 0.9900 |
| C1—C2 | 1.515 (2) | C13—H13A | 0.9800 |
| C1—H1A | 0.9900 | C13—H13B | 0.9800 |
| C1—H1B | 0.9900 | C13—H13C | 0.9800 |
| C2—C3 | 1.491 (2) | | |

| | | | |
|---------------|--------------|---------------|--------------|
| C4—S1—C3 | 91.75 (7) | C5—C6—C7 | 125.60 (13) |
| C10—S2—C11 | 85.86 (8) | N1—C7—C6 | 110.02 (11) |
| C11—S3—C12 | 102.89 (8) | N1—C7—H7A | 109.7 |
| C8—N1—C7 | 110.75 (11) | C6—C7—H7A | 109.7 |
| C8—N1—C1 | 111.43 (12) | N1—C7—H7B | 109.7 |
| C7—N1—C1 | 110.99 (12) | C6—C7—H7B | 109.7 |
| C9—N2—C10 | 123.21 (13) | H7A—C7—H7B | 108.2 |
| C9—N2—H2 | 117.7 (13) | N1—C8—C9 | 110.00 (13) |
| C10—N2—H2 | 119.1 (13) | N1—C8—H8A | 109.7 |
| C10—N3—N4 | 112.50 (12) | C9—C8—H8A | 109.7 |
| C11—N4—N3 | 111.23 (13) | N1—C8—H8B | 109.7 |
| N1—C1—C2 | 109.60 (13) | C9—C8—H8B | 109.7 |
| N1—C1—H1A | 109.8 | H8A—C8—H8B | 108.2 |
| C2—C1—H1A | 109.8 | O1—C9—N2 | 121.50 (15) |
| N1—C1—H1B | 109.8 | O1—C9—C8 | 122.81 (15) |
| C2—C1—H1B | 109.8 | N2—C9—C8 | 115.69 (13) |
| H1A—C1—H1B | 108.2 | N3—C10—N2 | 121.95 (13) |
| C3—C2—C1 | 108.17 (12) | N3—C10—S2 | 114.88 (12) |
| C3—C2—H2A | 110.1 | N2—C10—S2 | 123.17 (12) |
| C1—C2—H2A | 110.1 | N4—C11—S2 | 115.51 (12) |
| C3—C2—H2B | 110.1 | N4—C11—S3 | 126.62 (13) |
| C1—C2—H2B | 110.1 | S2—C11—S3 | 117.83 (9) |
| H2A—C2—H2B | 108.4 | C13—C12—S3 | 113.02 (12) |
| C6—C3—C2 | 124.21 (14) | C13—C12—H12A | 109.0 |
| C6—C3—S1 | 111.17 (12) | S3—C12—H12A | 109.0 |
| C2—C3—S1 | 124.61 (11) | C13—C12—H12B | 109.0 |
| C5—C4—S1 | 111.89 (12) | S3—C12—H12B | 109.0 |
| C5—C4—H4 | 124.1 | H12A—C12—H12B | 107.8 |
| S1—C4—H4 | 124.1 | C12—C13—H13A | 109.5 |
| C4—C5—C6 | 112.24 (14) | C12—C13—H13B | 109.5 |
| C4—C5—H5 | 123.9 | H13A—C13—H13B | 109.5 |
| C6—C5—H5 | 123.9 | C12—C13—H13C | 109.5 |
| C3—C6—C5 | 112.94 (14) | H13A—C13—H13C | 109.5 |
| C3—C6—C7 | 121.45 (13) | H13B—C13—H13C | 109.5 |
| C10—N3—N4—C11 | 0.50 (17) | C7—N1—C8—C9 | -70.74 (16) |
| C8—N1—C1—C2 | -165.54 (12) | C1—N1—C8—C9 | 165.18 (12) |
| C7—N1—C1—C2 | 70.53 (16) | C10—N2—C9—O1 | 2.6 (2) |
| N1—C1—C2—C3 | -49.63 (17) | C10—N2—C9—C8 | -178.09 (13) |
| C1—C2—C3—C6 | 16.2 (2) | N1—C8—C9—O1 | 100.49 (17) |
| C1—C2—C3—S1 | -165.28 (12) | N1—C8—C9—N2 | -78.85 (16) |
| C4—S1—C3—C6 | -0.65 (13) | N4—N3—C10—N2 | 178.63 (12) |
| C4—S1—C3—C2 | -179.37 (14) | N4—N3—C10—S2 | -1.53 (16) |
| C3—S1—C4—C5 | 0.16 (13) | C9—N2—C10—N3 | 175.29 (14) |
| S1—C4—C5—C6 | 0.36 (18) | C9—N2—C10—S2 | -4.5 (2) |
| C2—C3—C6—C5 | 179.69 (14) | C11—S2—C10—N3 | 1.57 (12) |
| S1—C3—C6—C5 | 0.97 (17) | C11—S2—C10—N2 | -178.59 (13) |
| C2—C3—C6—C7 | 0.9 (2) | N3—N4—C11—S2 | 0.73 (16) |
| S1—C3—C6—C7 | -177.84 (12) | N3—N4—C11—S3 | -176.86 (10) |
| C4—C5—C6—C3 | -0.9 (2) | C10—S2—C11—N4 | -1.29 (12) |

supplementary materials

| | | | |
|-------------|--------------|----------------|--------------|
| C4—C5—C6—C7 | 177.88 (15) | C10—S2—C11—S3 | 176.53 (10) |
| C8—N1—C7—C6 | -174.53 (12) | C12—S3—C11—N4 | -16.16 (16) |
| C1—N1—C7—C6 | -50.20 (16) | C12—S3—C11—S2 | 166.30 (9) |
| C3—C6—C7—N1 | 15.4 (2) | C11—S3—C12—C13 | -103.33 (14) |
| C5—C6—C7—N1 | -163.23 (14) | | |

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

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|-----------------------------------|----------|-------------|-------------|---------------|
| C12—H12B \cdots N1 ⁱ | 0.99 | 2.60 | 3.473 (3) | 147 |
| N2—H2 \cdots N3 ⁱⁱ | 0.89 (1) | 2.02 (1) | 2.902 (2) | 171.(2) |
| C5—H5 \cdots O1 ⁱⁱⁱ | 0.95 | 2.46 | 3.279 (2) | 145 |

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

Fig. 1

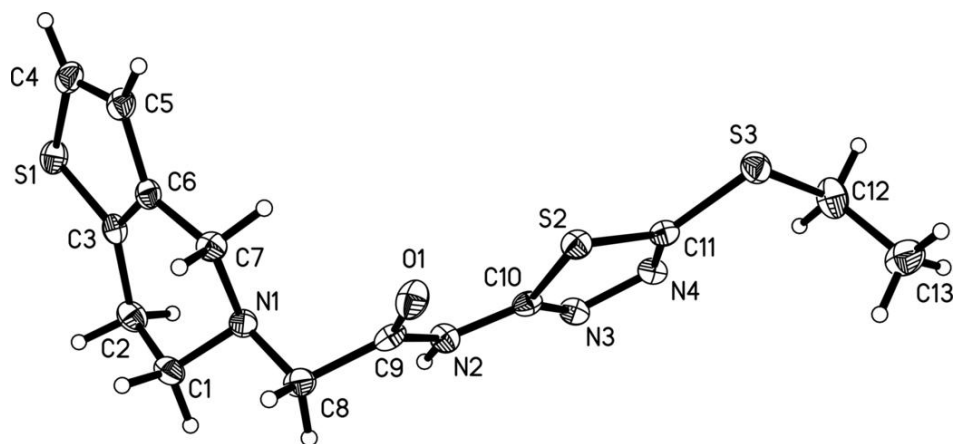


Fig. 2

