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2-(3,4-Dimethyl-5,5-dioxo-2H,4H-pyrazolo[4,3-c][1,2]benzothiazin-2-yl)-acetic acid

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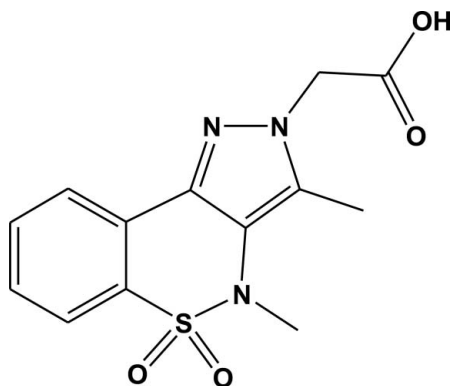
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Key indicators: single-crystal X-ray study; $T = 173$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å; R factor = 0.042; wR factor = 0.110; data-to-parameter ratio = 15.8.

In the title molecule, $\text{C}_{13}\text{H}_{13}\text{N}_3\text{O}_4\text{S}$, the heterocyclic thiazine ring adopts a half-chair conformation in which the S and an adjacent C atom are displaced by 0.919 (3) and 0.300 (4) Å, respectively, on the same side of the mean plane formed by the remaining ring atoms. The mean planes of the benzene and pyrazole rings are inclined at a dihedral angle of 18.32 (12) $^\circ$ with respect to each other. The acetate group is oriented at 80.75 (8) $^\circ$ with respect to the pyrazole ring. The crystal structure is stabilized by $\text{O}-\text{H}\cdots\text{N}$ and $\text{C}-\text{H}\cdots\text{O}$ hydrogen bonds, resulting in fused eight- and seven-membered rings with $R_2^2(8)$ and $R_2^2(7)$ graph-set motifs, respectively.

Related literature

For the biological activity of benzothiazine derivatives, see: Turck *et al.* (1996); Silverstein *et al.* (2000); Lombardino *et al.* (1973); Zinnes *et al.* (1973); Ahmad *et al.* (2010). For related structures, see: Siddiqui *et al.* (2008, 2009). For graph-set notation, see: Bernstein *et al.* (1995).



Experimental

Crystal data

$\text{C}_{13}\text{H}_{13}\text{N}_3\text{O}_4\text{S}$
 $M_r = 307.32$
 Monoclinic, $P2_1/n$
 $a = 10.495$ (4) Å
 $b = 8.415$ (2) Å
 $c = 15.136$ (6) Å
 $\beta = 91.034$ (19) $^\circ$
 $V = 1336.5$ (8) Å³
 $Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 0.26$ mm⁻¹
 $T = 173$ K
 $0.14 \times 0.12 \times 0.10$ mm

Data collection

Nonius KappaCCD diffractometer
 Absorption correction: multi-scan (SORTAV; Blessing, 1997)
 $T_{\min} = 0.964$, $T_{\max} = 0.974$
 5770 measured reflections
 3048 independent reflections
 2196 reflections with $I > \sigma(I)$
 $R_{\text{int}} = 0.033$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.042$
 $wR(F^2) = 0.110$
 $S = 1.03$
 3048 reflections
 193 parameters
 H-atom parameters constrained
 $\Delta\rho_{\max} = 0.25$ e Å⁻³
 $\Delta\rho_{\min} = -0.35$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, $^\circ$).

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|---|-------|-------------|-------------|---------------|
| $\text{O4}-\text{H4O}\cdots\text{N2}^i$ | 0.84 | 1.90 | 2.724 (2) | 165 |
| $\text{C9}-\text{H9A}\cdots\text{O2}^{ii}$ | 0.98 | 2.59 | 3.297 (3) | 129 |
| $\text{C5}-\text{H5}\cdots\text{O4}^{iii}$ | 0.95 | 2.59 | 3.476 (3) | 155 |
| $\text{C12}-\text{H12B}\cdots\text{O3}^{iii}$ | 0.99 | 2.35 | 3.303 (3) | 160 |

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

Data collection: COLLECT (Hooft, 1998); cell refinement: DENZO (Otwinowski & Minor, 1997); data reduction: SCALEPACK (Otwinowski & Minor, 1997); program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: ORTEP-3 for Windows (Farrugia, 1997); software used to prepare material for publication: SHELXL97.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: PK2415).

References

- Ahmad, M., Siddiqui, H. L., Zia-ur-Rehman, M. & Parvez, M. (2010). *Eur. J. Med. Chem.* **45**, 698–704.
 Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
 Blessing, R. H. (1997). *J. Appl. Cryst.* **30**, 421–426.
 Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
 Hooft, R. (1998). COLLECT. Nonius BV, Delft, The Netherlands.
 Lombardino, J. G., Wiseman, E. H. & Chiaini, J. (1973). *J. Med. Chem.* **16**, 493–496.
 Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.
 Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.

- Siddiqui, W. A., Ahmad, S., Tariq, M. I., Siddiqui, H. L. & Parvez, M. (2008). *Acta Cryst.* **C64**, o4–o6.
- Siddiqui, W. A., Siddiqui, H. L., Azam, M., Parvez, M. & Rizvi, U. F. (2009). *Acta Cryst.* **E65**, o2279–o2280.
- Silverstein, F. E., Faich, G., Goldstein, J. L., Simon, L. S., Pincus, T., Whelton, A., Makuch, R., Eisen, G., Agrawal, N. M., Stenson, W. F., Burr, A. M., Zhao, W. W., Kent, J. D., Lefkowitz, J. B., Verburg, K. M. & Geis, G. S. (2000). *J. Am. Med. Assoc.* **284**, 1247–1255.
- Turck, D., Roth, W. & Busch, U. (1996). *Br. J. Rheumatol.* **35**, 13–16.
- Zinnes, H., Lindo, N. A., Sircar, J. C., Schwartz, M. L. & Shavel, J. Jr (1973). *J. Med. Chem.* **16**, 44–48.

supporting information

Acta Cryst. (2012). E68, o1970–o1971 [doi:10.1107/S1600536812023677]

2-(3,4-Dimethyl-5,5-dioxo-2*H*,4*H*-pyrazolo[4,3-*c*][1,2]benzothiazin-2-yl)acetic acid

Sana Aslam, Hamid Latif Siddiqui, Matloob Ahmad, Muhammad Zia-ur-Rehman and Masood Parvez

S1. Comment

Meloxicam and Celecoxib are well known for their selective inhibition of the cox-2 enzyme that is responsible for inflammation (Turck *et al.*, 1996; Silverstein *et al.*, 2000). Though a number of benzothiazine based compounds have shown anti-inflammatory and analgesic character, yet there is a huge scope for selective cox-2 inhibitors in this family of heterocyclic compounds (Lombardino *et al.*, 1973; Zinnes *et al.*, 1973). In continuing the pursuit of potential drugs in this category, we have fused benzothiazine and pyrazole heterocycles that are core nuclei of meoxicam and celecoxib, respectively (Ahmad *et al.*, 2010), we have synthesized and determined the crystal structure of the title compound which is presented in this paper.

The bond distances and angles in the title compound (Fig. 1) agree very well with the corresponding bond distances and angles reported in closely related compounds (Siddiqui *et al.*, 2008; 2009). The heterocyclic thiazine ring adopts a twist chair conformation with atoms S1 and C1 displaced by 0.919 (3) and 0.300 (4) Å, respectively, on the same side of the mean plane formed by the remaining ring atoms (r.m.s. deviation 0.012 for N1/C6–C8 atoms). The mean-plane of the benzene ring C1–C6 makes a dihedral angle 18.32 (12)° with the mean-plane of the pyrazolyl ring (N2/N3/C7/C8/C10). The mean-plane of the acetate group (O3/O4/C12/C13) lies at 80.75 (8)° with respect to the pyrazolyl ring. The crystal structure is stabilized by intermolecular hydrogen bonding interactions (Fig. 2 and Table 1). The hydrogen bonds O4—H4O···N2 and C12—H12B···O3 result in eight membered rings with a $R_2^2(8)$ motif while C5—H5···O4 hydrogen bonding results in a seven membered ring with a $R_2^2(7)$ motif (Bernstein *et al.*, 1995); both rings are fused together and result in chains of molecules along the *b*-axis in a zigzag fashion. Moreover, C9—H9A···O2 interactions link the title molecules into chains along the *b*-axis further consolidating the crystal packing.

S2. Experimental

3,4-Dimethyl-2,4-dihydropyrazolo[4,3-*c*][1,2]benzothiazine 5,5-dioxide (5.0 g, 0.020 mole) and bromoacetic acid (3.31 g, 0.024 mole) were dissolved in anhydrous dimethyl formamide (15 ml) and anhydrous potassium carbonate (6.62 g, 0.048 mole) was added to it in small portions. The resulting reaction mixture was stirred for 2.5 h under a nitrogen atmosphere. The contents of the flask were poured over ice cold 10% HCl. Transparent crystals were grown from an aqueous solution, and were used for X-ray crystallographic studies.

S3. Refinement

All H atoms were positioned geometrically and refined using a riding model, with O—H = 0.84 Å and C—H = 0.95, 0.98 and 0.99 Å, for aryl, methyl and methylene H-atoms, respectively. The $U_{iso}(H)$ were included at $1.5U_{eq}(O)$ or $1.2U_{eq}(C)$.

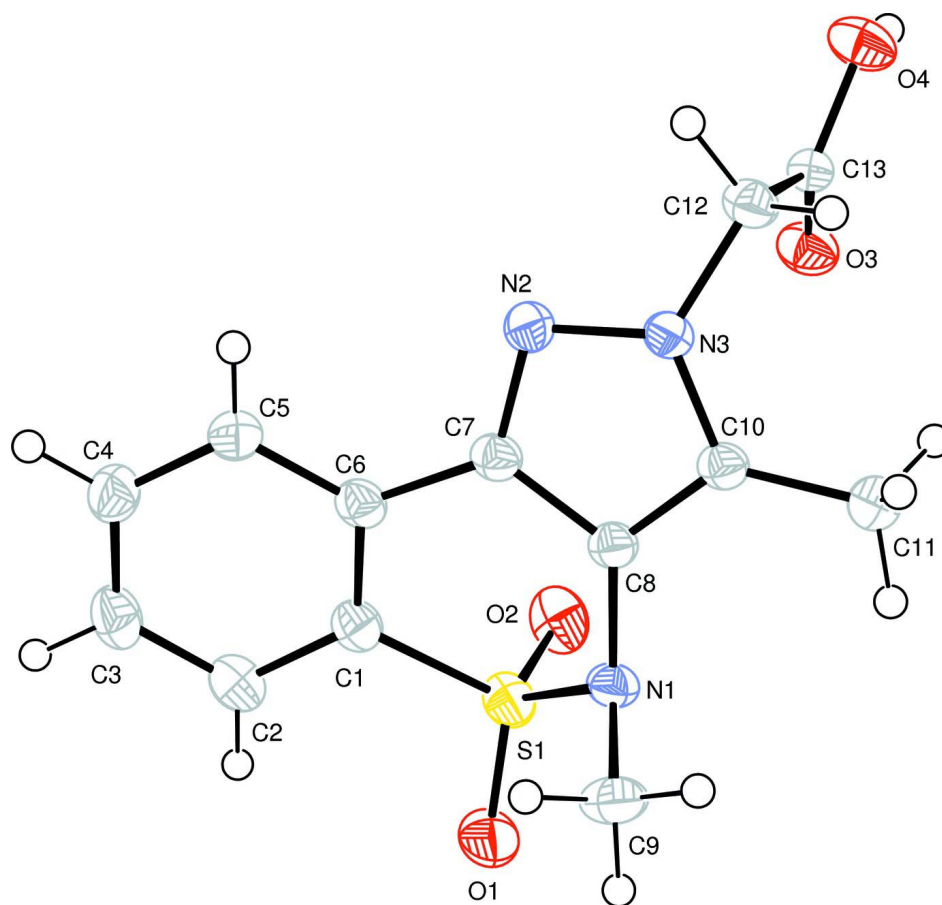


Figure 1

The molecular structure of the title compound with displacement ellipsoids drawn at the 50% probability level. H atoms are presented as small spheres of arbitrary radius.

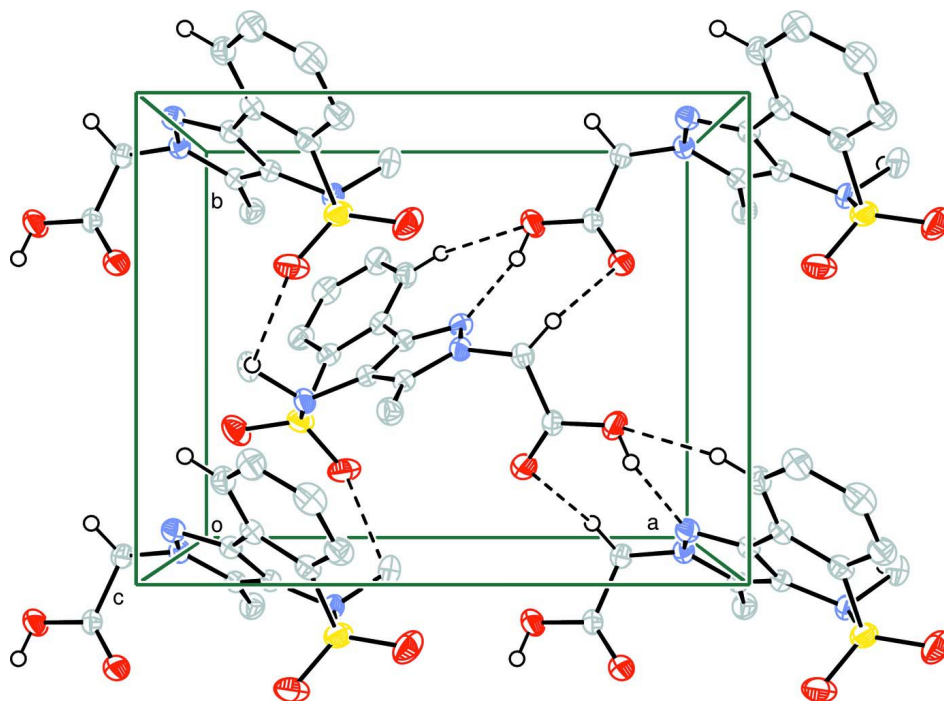


Figure 2

A view of the hydrogen bonding interactions (dotted lines) in the crystal structure of the title compound. H atoms not participating in hydrogen-bonding were omitted for clarity.

2-(3,4-Dimethyl-5,5-dioxo-2H,4H-pyrazolo[4,3-c][1,2]benzothiazin-2-yl)acetic acid

Crystal data

$C_{13}H_{13}N_3O_4S$

$M_r = 307.32$

Monoclinic, $P2_1/n$

Hall symbol: -P 2yn

$a = 10.495 (4) \text{ \AA}$

$b = 8.415 (2) \text{ \AA}$

$c = 15.136 (6) \text{ \AA}$

$\beta = 91.034 (19)^\circ$

$V = 1336.5 (8) \text{ \AA}^3$

$Z = 4$

$F(000) = 640$

$D_x = 1.527 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$

Cell parameters from 1947 reflections

$\theta = 1.0\text{--}27.5^\circ$

$\mu = 0.26 \text{ mm}^{-1}$

$T = 173 \text{ K}$

Block, colorless

$0.14 \times 0.12 \times 0.10 \text{ mm}$

Data collection

Nonius KappaCCD

diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

ω and φ scans

Absorption correction: multi-scan

(*SORTAV*; Blessing, 1997)

$T_{\min} = 0.964$, $T_{\max} = 0.974$

5770 measured reflections

3048 independent reflections

2196 reflections with $I > \sigma(I)$

$R_{\text{int}} = 0.033$

$\theta_{\max} = 27.5^\circ$, $\theta_{\min} = 4.1^\circ$

$h = -13 \rightarrow 13$

$k = -10 \rightarrow 10$

$l = -19 \rightarrow 19$

*Refinement*Refinement on F^2

Least-squares matrix: full

 $R[F^2 > 2\sigma(F^2)] = 0.042$ $wR(F^2) = 0.110$ $S = 1.03$

3048 reflections

193 parameters

0 restraints

Primary atom site location: structure-invariant
direct methodsSecondary atom site location: difference Fourier
map

Hydrogen site location: difference Fourier map

H-atom parameters constrained

 $w = 1/[\sigma^2(F_o^2) + (0.047P)^2 + 0.650P]$ where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\max} < 0.001$ $\Delta\rho_{\max} = 0.25 \text{ e } \text{\AA}^{-3}$ $\Delta\rho_{\min} = -0.35 \text{ e } \text{\AA}^{-3}$ *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)

| | x | y | z | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|-----|--------------|--------------|---------------|----------------------------------|
| S1 | 0.20345 (5) | 0.30572 (6) | 0.10421 (3) | 0.03013 (16) |
| O1 | 0.07080 (15) | 0.28041 (19) | 0.08552 (10) | 0.0419 (4) |
| O2 | 0.29133 (16) | 0.17922 (17) | 0.08858 (10) | 0.0392 (4) |
| O3 | 0.65265 (14) | 0.19936 (17) | 0.27745 (10) | 0.0328 (4) |
| O4 | 0.82589 (14) | 0.30151 (18) | 0.34514 (10) | 0.0344 (4) |
| H4O | 0.8579 | 0.2128 | 0.3330 | 0.052* |
| N1 | 0.21936 (16) | 0.35819 (19) | 0.20921 (10) | 0.0258 (4) |
| N2 | 0.52959 (16) | 0.54568 (18) | 0.19902 (10) | 0.0246 (4) |
| N3 | 0.52853 (15) | 0.48638 (19) | 0.28304 (10) | 0.0234 (4) |
| C1 | 0.25731 (19) | 0.4733 (2) | 0.04545 (12) | 0.0261 (4) |
| C2 | 0.1949 (2) | 0.5191 (2) | -0.03202 (13) | 0.0306 (5) |
| H2 | 0.1192 | 0.4665 | -0.0512 | 0.037* |
| C3 | 0.2448 (2) | 0.6428 (3) | -0.08089 (13) | 0.0344 (5) |
| H3 | 0.2035 | 0.6747 | -0.1344 | 0.041* |
| C4 | 0.3543 (2) | 0.7200 (3) | -0.05234 (13) | 0.0332 (5) |
| H4 | 0.3889 | 0.8027 | -0.0873 | 0.040* |
| C5 | 0.4142 (2) | 0.6782 (2) | 0.02673 (13) | 0.0284 (5) |
| H5 | 0.4883 | 0.7338 | 0.0464 | 0.034* |
| C6 | 0.36539 (19) | 0.5540 (2) | 0.07754 (12) | 0.0250 (4) |
| C7 | 0.41474 (19) | 0.5083 (2) | 0.16483 (12) | 0.0238 (4) |
| C8 | 0.34399 (18) | 0.4208 (2) | 0.22614 (12) | 0.0225 (4) |
| C9 | 0.1114 (2) | 0.4429 (3) | 0.25009 (15) | 0.0353 (5) |
| H9A | 0.1249 | 0.4473 | 0.3143 | 0.042* |
| H9B | 0.0318 | 0.3862 | 0.2366 | 0.042* |
| H9C | 0.1061 | 0.5512 | 0.2264 | 0.042* |

| | | | | |
|------|--------------|------------|--------------|------------|
| C10 | 0.41904 (18) | 0.4087 (2) | 0.30145 (12) | 0.0228 (4) |
| C11 | 0.3945 (2) | 0.3369 (2) | 0.38914 (13) | 0.0302 (5) |
| H11A | 0.3108 | 0.2851 | 0.3879 | 0.036* |
| H11B | 0.3958 | 0.4202 | 0.4344 | 0.036* |
| H11C | 0.4605 | 0.2580 | 0.4030 | 0.036* |
| C12 | 0.64872 (19) | 0.4694 (2) | 0.33106 (13) | 0.0262 (4) |
| H12A | 0.6344 | 0.4829 | 0.3951 | 0.031* |
| H12B | 0.7084 | 0.5533 | 0.3121 | 0.031* |
| C13 | 0.70744 (18) | 0.3072 (2) | 0.31454 (12) | 0.0226 (4) |

Atomic displacement parameters (Å²)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|-----|-------------|-------------|-------------|-------------|-------------|--------------|
| S1 | 0.0322 (3) | 0.0236 (3) | 0.0343 (3) | -0.0031 (2) | -0.0082 (2) | 0.0006 (2) |
| O1 | 0.0357 (9) | 0.0422 (9) | 0.0471 (9) | -0.0137 (7) | -0.0147 (7) | 0.0061 (7) |
| O2 | 0.0499 (11) | 0.0234 (8) | 0.0441 (9) | 0.0048 (7) | -0.0049 (7) | -0.0029 (6) |
| O3 | 0.0285 (8) | 0.0275 (7) | 0.0423 (8) | 0.0018 (6) | -0.0052 (7) | -0.0026 (7) |
| O4 | 0.0251 (8) | 0.0325 (8) | 0.0454 (9) | 0.0070 (6) | -0.0072 (7) | -0.0052 (7) |
| N1 | 0.0196 (9) | 0.0262 (8) | 0.0315 (9) | -0.0028 (7) | -0.0037 (7) | 0.0022 (7) |
| N2 | 0.0240 (9) | 0.0232 (8) | 0.0268 (8) | 0.0009 (7) | 0.0010 (7) | 0.0018 (7) |
| N3 | 0.0199 (9) | 0.0239 (8) | 0.0264 (8) | 0.0003 (7) | -0.0019 (6) | 0.0023 (7) |
| C1 | 0.0269 (12) | 0.0238 (10) | 0.0275 (10) | 0.0046 (8) | 0.0004 (8) | -0.0016 (8) |
| C2 | 0.0326 (13) | 0.0298 (11) | 0.0292 (10) | 0.0041 (9) | -0.0047 (9) | -0.0052 (9) |
| C3 | 0.0406 (14) | 0.0390 (12) | 0.0234 (9) | 0.0077 (10) | -0.0018 (9) | 0.0026 (9) |
| C4 | 0.0337 (13) | 0.0371 (12) | 0.0291 (10) | 0.0030 (10) | 0.0057 (9) | 0.0067 (9) |
| C5 | 0.0238 (11) | 0.0310 (11) | 0.0304 (10) | 0.0012 (9) | 0.0030 (8) | 0.0019 (9) |
| C6 | 0.0226 (11) | 0.0247 (10) | 0.0277 (9) | 0.0055 (8) | 0.0010 (8) | -0.0005 (8) |
| C7 | 0.0215 (11) | 0.0203 (9) | 0.0296 (10) | 0.0013 (8) | -0.0011 (8) | -0.0005 (8) |
| C8 | 0.0203 (10) | 0.0195 (9) | 0.0277 (9) | 0.0005 (8) | 0.0004 (8) | 0.0009 (8) |
| C9 | 0.0210 (11) | 0.0393 (12) | 0.0456 (12) | -0.0035 (9) | 0.0026 (9) | -0.0003 (10) |
| C10 | 0.0204 (10) | 0.0198 (9) | 0.0284 (9) | 0.0013 (8) | 0.0006 (8) | 0.0006 (8) |
| C11 | 0.0279 (12) | 0.0313 (11) | 0.0313 (10) | -0.0019 (9) | -0.0008 (9) | 0.0052 (9) |
| C12 | 0.0224 (11) | 0.0262 (10) | 0.0297 (10) | -0.0013 (8) | -0.0042 (8) | -0.0009 (8) |
| C13 | 0.0181 (10) | 0.0266 (10) | 0.0231 (9) | 0.0000 (8) | 0.0001 (7) | 0.0033 (8) |

Geometric parameters (Å, °)

| | | | |
|--------|-------------|--------|-----------|
| S1—O2 | 1.4309 (16) | C3—H3 | 0.9500 |
| S1—O1 | 1.4315 (17) | C4—C5 | 1.387 (3) |
| S1—N1 | 1.6550 (18) | C4—H4 | 0.9500 |
| S1—C1 | 1.765 (2) | C5—C6 | 1.401 (3) |
| O3—C13 | 1.207 (2) | C5—H5 | 0.9500 |
| O4—C13 | 1.320 (2) | C6—C7 | 1.462 (3) |
| O4—H4O | 0.8400 | C7—C8 | 1.407 (3) |
| N1—C8 | 1.429 (2) | C8—C10 | 1.378 (3) |
| N1—C9 | 1.483 (3) | C9—H9A | 0.9800 |
| N2—C7 | 1.341 (2) | C9—H9B | 0.9800 |
| N2—N3 | 1.366 (2) | C9—H9C | 0.9800 |

| | | | |
|--------------|--------------|---------------|--------------|
| N3—C10 | 1.355 (2) | C10—C11 | 1.485 (3) |
| N3—C12 | 1.452 (2) | C11—H11A | 0.9800 |
| C1—C2 | 1.388 (3) | C11—H11B | 0.9800 |
| C1—C6 | 1.401 (3) | C11—H11C | 0.9800 |
| C2—C3 | 1.385 (3) | C12—C13 | 1.520 (3) |
| C2—H2 | 0.9500 | C12—H12A | 0.9900 |
| C3—C4 | 1.383 (3) | C12—H12B | 0.9900 |
| O2—S1—O1 | 118.95 (10) | C1—C6—C7 | 117.20 (18) |
| O2—S1—N1 | 107.64 (9) | N2—C7—C8 | 110.47 (17) |
| O1—S1—N1 | 108.08 (10) | N2—C7—C6 | 126.05 (17) |
| O2—S1—C1 | 107.32 (10) | C8—C7—C6 | 123.45 (18) |
| O1—S1—C1 | 109.78 (9) | C10—C8—C7 | 106.48 (17) |
| N1—S1—C1 | 104.07 (9) | C10—C8—N1 | 128.98 (17) |
| C13—O4—H4O | 109.5 | C7—C8—N1 | 124.53 (17) |
| C8—N1—C9 | 116.85 (16) | N1—C9—H9A | 109.5 |
| C8—N1—S1 | 110.29 (13) | N1—C9—H9B | 109.5 |
| C9—N1—S1 | 117.66 (13) | H9A—C9—H9B | 109.5 |
| C7—N2—N3 | 104.55 (15) | N1—C9—H9C | 109.5 |
| C10—N3—N2 | 112.87 (15) | H9A—C9—H9C | 109.5 |
| C10—N3—C12 | 125.58 (16) | H9B—C9—H9C | 109.5 |
| N2—N3—C12 | 118.72 (15) | N3—C10—C8 | 105.57 (16) |
| C2—C1—C6 | 121.69 (19) | N3—C10—C11 | 122.79 (17) |
| C2—C1—S1 | 119.80 (16) | C8—C10—C11 | 131.57 (18) |
| C6—C1—S1 | 118.48 (15) | C10—C11—H11A | 109.5 |
| C3—C2—C1 | 118.9 (2) | C10—C11—H11B | 109.5 |
| C3—C2—H2 | 120.6 | H11A—C11—H11B | 109.5 |
| C1—C2—H2 | 120.6 | C10—C11—H11C | 109.5 |
| C4—C3—C2 | 120.44 (19) | H11A—C11—H11C | 109.5 |
| C4—C3—H3 | 119.8 | H11B—C11—H11C | 109.5 |
| C2—C3—H3 | 119.8 | N3—C12—C13 | 110.94 (15) |
| C3—C4—C5 | 120.8 (2) | N3—C12—H12A | 109.5 |
| C3—C4—H4 | 119.6 | C13—C12—H12A | 109.5 |
| C5—C4—H4 | 119.6 | N3—C12—H12B | 109.5 |
| C4—C5—C6 | 119.9 (2) | C13—C12—H12B | 109.5 |
| C4—C5—H5 | 120.1 | H12A—C12—H12B | 108.0 |
| C6—C5—H5 | 120.1 | O3—C13—O4 | 125.03 (18) |
| C5—C6—C1 | 118.26 (18) | O3—C13—C12 | 124.07 (17) |
| C5—C6—C7 | 124.43 (18) | O4—C13—C12 | 110.90 (16) |
| O2—S1—N1—C8 | 64.00 (15) | N3—N2—C7—C6 | 176.09 (18) |
| O1—S1—N1—C8 | -166.34 (12) | C5—C6—C7—N2 | -18.7 (3) |
| C1—S1—N1—C8 | -49.68 (15) | C1—C6—C7—N2 | 165.16 (18) |
| O2—S1—N1—C9 | -158.49 (15) | C5—C6—C7—C8 | 159.33 (19) |
| O1—S1—N1—C9 | -28.84 (17) | C1—C6—C7—C8 | -16.8 (3) |
| C1—S1—N1—C9 | 87.83 (16) | N2—C7—C8—C10 | 1.5 (2) |
| C7—N2—N3—C10 | 2.1 (2) | C6—C7—C8—C10 | -176.80 (17) |
| C7—N2—N3—C12 | 164.15 (16) | N2—C7—C8—N1 | -177.84 (17) |

| | | | |
|-------------|--------------|----------------|--------------|
| O2—S1—C1—C2 | 105.04 (18) | C6—C7—C8—N1 | 3.8 (3) |
| O1—S1—C1—C2 | -25.6 (2) | C9—N1—C8—C10 | 76.3 (3) |
| N1—S1—C1—C2 | -141.05 (16) | S1—N1—C8—C10 | -145.81 (18) |
| O2—S1—C1—C6 | -73.08 (18) | C9—N1—C8—C7 | -104.5 (2) |
| O1—S1—C1—C6 | 156.31 (16) | S1—N1—C8—C7 | 33.4 (2) |
| N1—S1—C1—C6 | 40.84 (18) | N2—N3—C10—C8 | -1.2 (2) |
| C6—C1—C2—C3 | 3.3 (3) | C12—N3—C10—C8 | -161.78 (17) |
| S1—C1—C2—C3 | -174.78 (15) | N2—N3—C10—C11 | -178.68 (17) |
| C1—C2—C3—C4 | -0.6 (3) | C12—N3—C10—C11 | 20.8 (3) |
| C2—C3—C4—C5 | -1.8 (3) | C7—C8—C10—N3 | -0.2 (2) |
| C3—C4—C5—C6 | 1.5 (3) | N1—C8—C10—N3 | 179.14 (18) |
| C4—C5—C6—C1 | 1.1 (3) | C7—C8—C10—C11 | 177.0 (2) |
| C4—C5—C6—C7 | -175.00 (19) | N1—C8—C10—C11 | -3.7 (4) |
| C2—C1—C6—C5 | -3.5 (3) | C10—N3—C12—C13 | 70.0 (2) |
| S1—C1—C6—C5 | 174.58 (15) | N2—N3—C12—C13 | -89.5 (2) |
| C2—C1—C6—C7 | 172.87 (18) | N3—C12—C13—O3 | -10.2 (3) |
| S1—C1—C6—C7 | -9.0 (2) | N3—C12—C13—O4 | 168.99 (16) |
| N3—N2—C7—C8 | -2.2 (2) | | |

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> |
|------------------------------|-------------|---------------|-----------------------|-------------------------|
| O4—H4O...N2 ⁱ | 0.84 | 1.90 | 2.724 (2) | 165 |
| C9—H9A...O2 ⁱⁱ | 0.98 | 2.59 | 3.297 (3) | 129 |
| C5—H5...O4 ⁱⁱⁱ | 0.95 | 2.59 | 3.476 (3) | 155 |
| C12—H12B...O3 ⁱⁱⁱ | 0.99 | 2.35 | 3.303 (3) | 160 |
| C9—H9B...O1 | 0.98 | 2.49 | 2.867 (3) | 102 |

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