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# 2-Methyl-4-oxo-6,7,8,9-tetrahydrothieno[2′,3′:4,5]pyrimidino[1,2-*a*]pyridine-3-carboxylic acid

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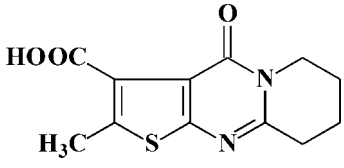
Key indicators: single-crystal X-ray study; $T$ = 296 K; mean $\sigma$(C–C) = 0.007 Å; disorder in main residue; $R$ factor = 0.063; $wR$ factor = 0.169; data-to-parameter ratio = 9.9.

There are two independent molecules in the asymmetric unit of the title compound, $C_{12}H_{12}N_2O_3S$. With the exception of the methylene groups, a mean plane fitted through all non-H atoms of each molecule has an r.m.s. deviation of 0.035 Å for one molecule and 0.120 Å for the second. In one of the independent molecules, the methylene groups was refined using a disorder model with an occupancy ratio of 0.53:0.47 (14). Each molecule features an intramolecular O—H···O hydrogen bond, which generates an $S$(7) ring.

## Related literature

For the synthesis of thieno[2,3-*d*]pyrimidin-4-ones and their derivatives, see: Litvinov (2004); Elmuradov *et al.* (2010); Csukonyi *et al.* (1986). For the physiological activity of thieno[2,3-*d*]pyrimidin-4-ones and their derivatives, see: Lilienkampf *et al.* (2007). For a related structure, see: Bozorov *et al.* (2010). For hydrogen-bond motifs, see: Bernstein *et al.* (1995).




## Experimental

### Crystal data

$C_{12}H_{12}N_2O_3S$ $M_r$ = 264.30
Monoclinic, $P2_1/n$
$a$ = 7.2550 (15) Å
$b$ = 20.506 (4) Å
$c$ = 15.824 (3) Å
$\beta$ = 96.93 (3)°
$V$ = 2337.0 (8) Å$^3$
$Z$ = 8
Cu $K\alpha$ radiation
$\mu$ = 2.50 mm$^{-1}$
$T$ = 296 K
0.60 × 0.40 × 0.15 mm

### Data collection

Stoe STADI4 diffractometer
Absorption correction: $\psi$ scan (Blessing, 1987)
$T_{min}$ = 0.346, $T_{max}$ = 0.687
4297 measured reflections
3438 independent reflections
2420 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.047
$\theta_{max}$ = 60.0°
3 standard reflections every 60 min
intensity decay: 4.7%

### Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.063
$wR(F^2)$ = 0.169
$S$ = 1.10
3438 reflections
348 parameters
23 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.20 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.28 e Å$^{-3}$

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| O2—H2*O*···O1 | 0.87 (2) | 1.63 (2) | 2.501 (5) | 177 (7) |
| O52—H52*O*···O51 | 0.87 (2) | 1.71 (3) | 2.518 (6) | 154 (4) |

Data collection: *STADI4* (Stoe & Cie, 1997); cell refinement: *STADI4*; data reduction: *X-RED* (Stoe & Cie, 1997); 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: *publCIF* (Westrip, 2010).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: NK2082).

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# supporting information

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## 2-Methyl-4-oxo-6,7,8,9-tetrahydrothieno[2′,3′:4,5]pyrimidino[1,2-*a*]pyridine-3-carboxylic acid

**Burkhon Zh. Elmuradov, Khurshed A. Bozorov, Rasul Ya. Okmanov, Bakhodir Tashkhodjaev and Khusnutdin M. Shakhidoyatov**

### S1. Comment

Among heterocyclic compounds. the thieno[2,3-*d*]pyrimidin-4-one family (Litvinov, 2004; Elmuradov *et al.*, 2010; Csukonyi *et al.*, 1986) has been shown to possess various physiological activity (Lilienkampf *et al.*, 2007). The reaction of 2,3-dimethylthieno[2′,3′:4,5]pyrimidino[1,2-*a*]pyridin-4-one with nitric acid in ratio of reagents - substrate:$HNO_3$ - 1:4 in concentrated sulfuric acid leads to the formation of 3-hydroxycarbonyl-2- methylthieno[2′,3′:4,5]pyrimidino[1,2-*a*]pyridin-4-one (Figure 1). We report here the synthesis and crystal structure.

The asymmetric unit contains two crystallographically unique molecules (Figure 2). With the exception of the methylene group, a mean plane fitted through all non-H atoms of each molecule has an rms deviation of 0.035 for one molecule, and 0.120 for the second. In one of the unique molecules the methylene group was refined using a disorder model with an occupancy ratio of 0.53:0.47 (14). An S(7) intramolecular O—H···O hydrogen bond is observed in each unique molecule (Bernstein *et al.*, 1995).

### S2. Experimental

Into a flask supplied with a mixer was poured 2 ml $H_2SO_4$ and cooled by an ice bath (0.25 h). Then 1 g (4.26 mmole) 2,3-dimethylthieno[2′,3′:4,5]pyrimidino[1,2-*a*]pyridin-4-one was added in portions, mixed before complete dissolution, nitrating acid consisting of 1.89 g (1.4 ml, d═1.35 g/ml) (17.08 mmole) $HNO_3$ and 1.4 ml (d═1.835 g/ml) $H_2SO_4$ were added (0.5 h) drop wise. A reactionary mixture were mixed 1 h at room temperature and left 2 days at room temperature and a mixture is decomposed in cold. The formed yellow crystals were filtered off and washed with water and dried. Yield 1.0 g (89%), m.p. 478–479 K (ethanol). The yellow crystals suitable for X-ray analysis were obtained from absolute methanol at room temperature.

### S3. Refinement

C-bound H atoms were placed geometrically (with C—H distances of 0.97 Å for $CH_2$; 0.96 Å for $CH_3$; and 0.93 Å for $C_{ar}$) and included in the refinement in a riding motion approximation with $U_{iso}$=1.2$U_{eq}$(C) [$U_{iso}$=1.5$U_{eq}$(C) for methyl H atoms]. O-bound H atoms involved in the intermolecular hydrogen bonding were found by difference Fourier synthesis and refined isotropically with a distance restrains of 0.85 (2) Å. [O2—H2O = 0.870 (20) Å, O52—H52O = 0.871 (19) Å]. Atoms C56, C57, C58 and C59 were refined using a disorder model with an occupancy ratio of 0.53:0.47 (14)

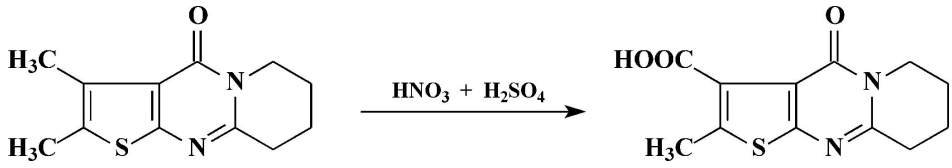


**Figure 1**

Reaction scheme.

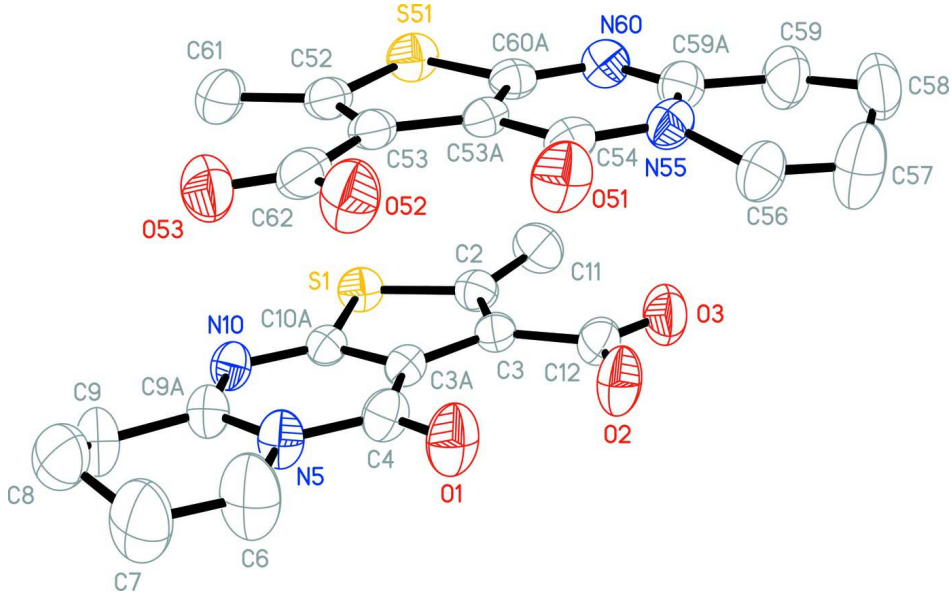


**Figure 2**

The asymmetric unit of the title compound, with H atoms and the minor disorder component omitted. Displacement ellipsoids are at the 30% probability level.

### 2-Methyl-4-oxo-6,7,8,9-tetrahydrothieno[2′,3′:4,5]pyrimidino[1,2- *a*]pyridine-3-carboxylic acid

*Crystal data*

$C_{12}H_{12}N_2O_3S$
$M_r = 264.30$
Monoclinic, $P2_1/n$
Hall symbol: -P 2yn
$a = 7.2550\ (15)$ Å
$b = 20.506\ (4)$ Å
$c = 15.824\ (3)$ Å
$\beta = 96.93\ (3)°$
$V = 2337.0\ (8)$ Å$^3$
$Z = 8$
$F(000) = 1104$
$D_x = 1.502$ Mg m$^{-3}$
Cu $K\alpha$ radiation, $\lambda = 1.54184$ Å
Cell parameters from 12 reflections
$\theta = 10–20°$
$\mu = 2.50$ mm$^{-1}$
$T = 296$ K
Prism, yellow
0.60 × 0.40 × 0.15 mm

*Data collection*

Stoe STADI4 diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
Scan width ($\omega$) = 1.56 – 1.80, scan ratio $2\theta$:$\omega$ = 1.00 I(Net) and sigma(I) calculated according to Blessing (1987)
Absorption correction: $\psi$ scan (Blessing, 1987)
$T_{min} = 0.346$, $T_{max} = 0.687$
4297 measured reflections
3438 independent reflections
2420 reflections with $I > 2\sigma(I)$
$R_{int} = 0.047$

$\theta_{max}$ = 60.0°, $\theta_{min}$ = 3.5°
$h$ = −8→8
$k$ = 0→23
$l$ = 0→17
3 standard reflections every 60 min
intensity decay: 4.7%

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.063
$wR(F^2)$ = 0.169
$S$ = 1.10
3438 reflections
348 parameters
23 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0601P)^2 + 2.3488P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.20 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.28 e Å$^{-3}$
Extinction correction: *SHELXL*, $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.0018 (3)

*Special details*

**Experimental**. $\psi$ Scan Reflections used $\mu$ * R = 0.00
H K L, $\theta$, $\chi$, $I_{min}/I_{max}$: -1 -1 0 13.0 84.8 0.563
**$^1$H NMR (400 MHz, $CDCl_3$):** 15.46 (1*H*, s, OH), 4.06 (2*H*, t, J=6.1 Hz, H-6), 3.01 (2*H*, t, J=6.6 Hz, H-9), 2.76 (3*H*, s, $CH_3$-2), 1.93–2.07 (4*H*, m, H-7, 8).

**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.

**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 $F^2 > 2$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 (Å$^2$)*

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ | Occ. (<1) |
|---|---|---|---|---|---|
| S1 | 0.04758 (17) | 0.79444 (6) | 0.42793 (7) | 0.0671 (4) | |
| O1 | 0.2734 (6) | 0.78157 (17) | 0.7344 (2) | 0.0980 (12) | |
| O2 | 0.3136 (6) | 0.66799 (17) | 0.6820 (3) | 0.0995 (13) | |
| H2O | 0.304 (9) | 0.7074 (15) | 0.701 (4) | 0.119* | |
| O3 | 0.2595 (6) | 0.61070 (18) | 0.5666 (3) | 0.1034 (13) | |
| N5 | 0.1590 (6) | 0.87759 (18) | 0.6804 (2) | 0.0722 (11) | |
| N10 | 0.0491 (5) | 0.89415 (17) | 0.5367 (2) | 0.0619 (10) | |
| C2 | 0.1269 (6) | 0.7205 (2) | 0.4683 (3) | 0.0651 (12) | |
| C3 | 0.1810 (6) | 0.7225 (2) | 0.5538 (3) | 0.0580 (11) | |
| C3A | 0.1573 (5) | 0.7869 (2) | 0.5876 (2) | 0.0538 (10) | |
| C4 | 0.2008 (7) | 0.8123 (2) | 0.6711 (3) | 0.0680 (13) | |
| C6 | 0.2045 (12) | 0.9053 (3) | 0.7664 (3) | 0.132 (3) | |
| H6A | 0.1358 | 0.8810 | 0.8048 | 0.159* | |
| H6B | 0.3354 | 0.8977 | 0.7841 | 0.159* | |
| C7 | 0.1711 (14) | 0.9690 (3) | 0.7773 (4) | 0.146 (3) | |
| H7A | 0.2672 | 0.9851 | 0.8202 | 0.175* | |

| | | | | | |
|---|---|---|---|---|---|
| H7B | 0.0546 | 0.9722 | 0.8013 | 0.175* | |
| C8 | 0.1608 (11) | 1.0132 (3) | 0.7067 (4) | 0.114 (2) | |
| H8A | 0.2849 | 1.0221 | 0.6927 | 0.136* | |
| H8B | 0.1070 | 1.0542 | 0.7223 | 0.136* | |
| C9 | 0.0451 (9) | 0.9853 (2) | 0.6305 (4) | 0.0967 (18) | |
| H9A | −0.0848 | 0.9889 | 0.6388 | 0.116* | |
| H9B | 0.0642 | 1.0110 | 0.5809 | 0.116* | |
| C9A | 0.0868 (7) | 0.9159 (2) | 0.6132 (3) | 0.0679 (12) | |
| C10A | 0.0859 (6) | 0.8302 (2) | 0.5262 (2) | 0.0533 (10) | |
| C11 | 0.1308 (8) | 0.6661 (3) | 0.4061 (3) | 0.0911 (17) | |
| H11A | 0.2570 | 0.6528 | 0.4036 | 0.137* | |
| H11B | 0.0770 | 0.6804 | 0.3509 | 0.137* | |
| H11C | 0.0610 | 0.6299 | 0.4239 | 0.137* | |
| C12 | 0.2532 (7) | 0.6630 (3) | 0.6007 (4) | 0.0745 (14) | |
| S51 | 0.54855 (18) | 0.78491 (7) | 0.40855 (7) | 0.0753 (4) | |
| O51 | 0.7745 (6) | 0.74580 (18) | 0.71060 (19) | 0.0938 (12) | |
| O52 | 0.7039 (7) | 0.8660 (2) | 0.7032 (3) | 0.1067 (14) | |
| H52O | 0.756 (9) | 0.8281 (18) | 0.715 (4) | 0.129* | |
| O53 | 0.5648 (7) | 0.9368 (2) | 0.6164 (3) | 0.1136 (15) | |
| N55 | 0.7534 (5) | 0.65997 (19) | 0.6203 (2) | 0.0672 (10) | |
| N60 | 0.6566 (5) | 0.66871 (19) | 0.4739 (2) | 0.0684 (10) | |
| C52 | 0.5490 (6) | 0.8492 (2) | 0.4774 (3) | 0.0683 (13) | |
| C53A | 0.6617 (5) | 0.7637 (2) | 0.5653 (2) | 0.0535 (10) | |
| C53 | 0.6134 (6) | 0.8322 (2) | 0.5592 (3) | 0.0615 (11) | |
| C54 | 0.7323 (6) | 0.7256 (2) | 0.6369 (3) | 0.0642 (12) | |
| C56 | 0.792 (9) | 0.6213 (13) | 0.7004 (13) | 0.089 (7) | 0.468 (14) |
| H56A | 0.9111 | 0.6347 | 0.7298 | 0.106* | 0.468 (14) |
| H56B | 0.6979 | 0.6312 | 0.7370 | 0.106* | 0.468 (14) |
| C57 | 0.795 (7) | 0.5546 (14) | 0.6872 (16) | 0.138 (8) | 0.468 (14) |
| H57A | 0.6742 | 0.5381 | 0.6969 | 0.166* | 0.468 (14) |
| H57B | 0.8840 | 0.5366 | 0.7319 | 0.166* | 0.468 (14) |
| C58 | 0.838 (3) | 0.5262 (9) | 0.6076 (14) | 0.104 (4) | 0.468 (14) |
| H58A | 0.8013 | 0.4807 | 0.6053 | 0.125* | 0.468 (14) |
| H58B | 0.9703 | 0.5285 | 0.6050 | 0.125* | 0.468 (14) |
| C59 | 0.737 (8) | 0.5619 (7) | 0.5322 (15) | 0.107 (3) | 0.468 (14) |
| H59A | 0.8012 | 0.5534 | 0.4832 | 0.129* | 0.468 (14) |
| H59B | 0.6134 | 0.5432 | 0.5203 | 0.129* | 0.468 (14) |
| C56′ | 0.832 (7) | 0.6170 (11) | 0.6917 (12) | 0.089 (7) | 0.532 (14) |
| H56C | 0.9576 | 0.6318 | 0.7108 | 0.106* | 0.532 (14) |
| H56D | 0.7597 | 0.6230 | 0.7387 | 0.106* | 0.532 (14) |
| C57′ | 0.840 (6) | 0.5505 (13) | 0.6745 (15) | 0.138 (8) | 0.532 (14) |
| H57C | 0.8124 | 0.5275 | 0.7251 | 0.166* | 0.532 (14) |
| H57D | 0.9668 | 0.5401 | 0.6665 | 0.166* | 0.532 (14) |
| C58′ | 0.719 (3) | 0.5234 (7) | 0.6019 (12) | 0.104 (4) | 0.532 (14) |
| H58C | 0.5906 | 0.5249 | 0.6130 | 0.125* | 0.532 (14) |
| H58D | 0.7519 | 0.4782 | 0.5932 | 0.125* | 0.532 (14) |
| C59′ | 0.744 (7) | 0.5631 (6) | 0.5233 (13) | 0.107 (3) | 0.532 (14) |
| H59C | 0.8676 | 0.5563 | 0.5077 | 0.129* | 0.532 (14) |

| | | | | | |
|---|---|---|---|---|---|
| H59D | 0.6549 | 0.5490 | 0.4762 | 0.129* | 0.532 (14) |
| C59A | 0.7158 (7) | 0.6339 (2) | 0.5402 (3) | 0.0706 (13) | |
| C60A | 0.6315 (6) | 0.7326 (2) | 0.4885 (3) | 0.0587 (11) | |
| C61 | 0.4852 (9) | 0.9139 (3) | 0.4415 (4) | 0.0991 (19) | |
| H61A | 0.3715 | 0.9259 | 0.4628 | 0.149* | |
| H61B | 0.4649 | 0.9112 | 0.3805 | 0.149* | |
| H61C | 0.5783 | 0.9462 | 0.4582 | 0.149* | |
| C62 | 0.6225 (8) | 0.8821 (3) | 0.6276 (4) | 0.0836 (15) | |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| S1 | 0.0690 (8) | 0.0763 (8) | 0.0541 (6) | 0.0001 (6) | 0.0000 (5) | 0.0014 (6) |
| O1 | 0.138 (3) | 0.083 (2) | 0.064 (2) | 0.010 (2) | −0.025 (2) | 0.0097 (18) |
| O2 | 0.132 (3) | 0.069 (2) | 0.091 (3) | 0.012 (2) | −0.014 (2) | 0.020 (2) |
| O3 | 0.135 (4) | 0.062 (2) | 0.114 (3) | 0.012 (2) | 0.018 (2) | 0.004 (2) |
| N5 | 0.094 (3) | 0.060 (2) | 0.058 (2) | 0.001 (2) | −0.009 (2) | −0.0030 (18) |
| N10 | 0.065 (2) | 0.056 (2) | 0.062 (2) | 0.0013 (18) | −0.0050 (18) | 0.0081 (18) |
| C2 | 0.062 (3) | 0.065 (3) | 0.068 (3) | −0.006 (2) | 0.011 (2) | −0.007 (2) |
| C3 | 0.051 (3) | 0.056 (3) | 0.069 (3) | −0.001 (2) | 0.012 (2) | 0.004 (2) |
| C3A | 0.050 (2) | 0.056 (3) | 0.054 (2) | −0.004 (2) | 0.0020 (18) | 0.006 (2) |
| C4 | 0.076 (3) | 0.066 (3) | 0.058 (3) | −0.004 (2) | −0.004 (2) | 0.006 (2) |
| C6 | 0.230 (9) | 0.094 (5) | 0.064 (4) | 0.010 (5) | −0.022 (4) | −0.022 (3) |
| C7 | 0.252 (11) | 0.097 (5) | 0.089 (5) | −0.004 (6) | 0.016 (5) | −0.026 (4) |
| C8 | 0.164 (7) | 0.083 (4) | 0.097 (4) | −0.021 (4) | 0.030 (4) | −0.023 (4) |
| C9 | 0.115 (5) | 0.058 (3) | 0.112 (4) | 0.006 (3) | −0.008 (4) | −0.001 (3) |
| C9A | 0.072 (3) | 0.055 (3) | 0.074 (3) | 0.002 (2) | −0.003 (2) | 0.002 (2) |
| C10A | 0.048 (2) | 0.056 (3) | 0.055 (2) | −0.003 (2) | 0.0022 (18) | 0.003 (2) |
| C11 | 0.100 (4) | 0.091 (4) | 0.083 (4) | 0.001 (3) | 0.010 (3) | −0.018 (3) |
| C12 | 0.071 (3) | 0.061 (3) | 0.093 (4) | −0.004 (3) | 0.014 (3) | 0.011 (3) |
| S51 | 0.0716 (8) | 0.0943 (10) | 0.0577 (7) | 0.0027 (7) | −0.0013 (6) | 0.0137 (6) |
| O51 | 0.132 (3) | 0.094 (3) | 0.0509 (19) | −0.001 (2) | −0.0072 (19) | 0.0014 (18) |
| O52 | 0.162 (4) | 0.082 (3) | 0.076 (3) | −0.003 (3) | 0.016 (3) | −0.009 (2) |
| O53 | 0.153 (4) | 0.072 (3) | 0.121 (3) | 0.013 (3) | 0.041 (3) | −0.002 (2) |
| N55 | 0.072 (3) | 0.067 (3) | 0.062 (2) | −0.003 (2) | 0.0049 (19) | 0.0116 (19) |
| N60 | 0.075 (3) | 0.068 (3) | 0.062 (2) | −0.006 (2) | 0.0056 (19) | −0.008 (2) |
| C52 | 0.058 (3) | 0.078 (3) | 0.070 (3) | 0.002 (2) | 0.014 (2) | 0.014 (2) |
| C53A | 0.047 (2) | 0.062 (3) | 0.052 (2) | −0.006 (2) | 0.0081 (19) | 0.005 (2) |
| C53 | 0.055 (3) | 0.066 (3) | 0.066 (3) | −0.007 (2) | 0.019 (2) | 0.000 (2) |
| C54 | 0.063 (3) | 0.073 (3) | 0.056 (3) | −0.007 (2) | 0.008 (2) | 0.004 (2) |
| C56 | 0.105 (19) | 0.086 (5) | 0.074 (5) | 0.014 (6) | 0.009 (7) | 0.031 (4) |
| C57 | 0.202 (19) | 0.090 (6) | 0.116 (9) | 0.012 (8) | −0.011 (10) | 0.030 (6) |
| C58 | 0.107 (10) | 0.064 (4) | 0.138 (7) | 0.019 (9) | 0.005 (12) | 0.012 (5) |
| C59 | 0.147 (7) | 0.059 (4) | 0.120 (6) | 0.002 (4) | 0.030 (6) | −0.002 (4) |
| C56′ | 0.105 (19) | 0.086 (5) | 0.074 (5) | 0.014 (6) | 0.009 (7) | 0.031 (4) |
| C57′ | 0.202 (19) | 0.090 (6) | 0.116 (9) | 0.012 (8) | −0.011 (10) | 0.030 (6) |
| C58′ | 0.107 (10) | 0.064 (4) | 0.138 (7) | 0.019 (9) | 0.005 (12) | 0.012 (5) |
| C59′ | 0.147 (7) | 0.059 (4) | 0.120 (6) | 0.002 (4) | 0.030 (6) | −0.002 (4) |

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|---|---|---|---|---|---|---|
| C59A | 0.073 (3) | 0.064 (3) | 0.075 (3) | −0.004 (2) | 0.009 (3) | −0.001 (3) |
| C60A | 0.047 (2) | 0.075 (3) | 0.054 (2) | −0.003 (2) | 0.0043 (19) | 0.004 (2) |
| C61 | 0.107 (5) | 0.085 (4) | 0.108 (4) | 0.012 (3) | 0.024 (3) | 0.039 (3) |
| C62 | 0.090 (4) | 0.080 (4) | 0.085 (4) | −0.013 (3) | 0.027 (3) | 0.005 (3) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| S1—C10A | 1.712 (4) | N55—C54 | 1.382 (6) |
| S1—C2 | 1.717 (5) | N55—C56 | 1.492 (13) |
| O1—C4 | 1.245 (5) | N55—C56′ | 1.492 (12) |
| O2—C12 | 1.313 (6) | N60—C59A | 1.299 (6) |
| O2—H2O | 0.87 (2) | N60—C60A | 1.346 (6) |
| O3—C12 | 1.204 (6) | C52—C53 | 1.367 (6) |
| N5—C9A | 1.374 (5) | C52—C61 | 1.495 (6) |
| N5—C4 | 1.384 (6) | C53A—C60A | 1.368 (5) |
| N5—C6 | 1.474 (6) | C53A—C54 | 1.420 (6) |
| N10—C9A | 1.288 (5) | C53A—C53 | 1.447 (6) |
| N10—C10A | 1.352 (5) | C53—C62 | 1.485 (7) |
| C2—C3 | 1.363 (6) | C54—O51 | 1.241 (5) |
| C2—C11 | 1.491 (6) | C56—C57 | 1.385 (13) |
| C3—C3A | 1.444 (6) | C56—H56A | 0.9700 |
| C3—C12 | 1.489 (6) | C56—H56B | 0.9700 |
| C3A—C10A | 1.370 (5) | C57—C58 | 1.45 (2) |
| C3A—C4 | 1.421 (6) | C57—H57A | 0.9700 |
| C4—O1 | 1.245 (5) | C57—H57B | 0.9700 |
| C6—C7 | 1.342 (7) | C58—C59 | 1.512 (18) |
| C6—H6A | 0.9700 | C58—H58A | 0.9700 |
| C6—H6B | 0.9700 | C58—H58B | 0.9700 |
| C7—C8 | 1.435 (8) | C59—C59A | 1.490 (13) |
| C7—H7A | 0.9700 | C59—H59A | 0.9700 |
| C7—H7B | 0.9700 | C59—H59B | 0.9700 |
| C8—C9 | 1.498 (7) | C56′—C57′ | 1.392 (12) |
| C8—H8A | 0.9700 | C56′—H56C | 0.9700 |
| C8—H8B | 0.9700 | C56′—H56D | 0.9700 |
| C9—C9A | 1.487 (6) | C57′—C58′ | 1.47 (2) |
| C9—H9A | 0.9700 | C57′—H57C | 0.9700 |
| C9—H9B | 0.9700 | C57′—H57D | 0.9700 |
| C11—H11A | 0.9600 | C58′—C59′ | 1.516 (18) |
| C11—H11B | 0.9600 | C58′—H58C | 0.9700 |
| C11—H11C | 0.9600 | C58′—H58D | 0.9700 |
| S51—C52 | 1.709 (5) | C59′—C59A | 1.494 (12) |
| S51—C60A | 1.711 (4) | C59′—H59C | 0.9700 |
| O51—C54 | 1.241 (5) | C59′—H59D | 0.9700 |
| O52—C62 | 1.312 (7) | C61—H61A | 0.9600 |
| O52—H52O | 0.871 (19) | C61—H61B | 0.9600 |
| O53—C62 | 1.202 (6) | C61—H61C | 0.9600 |
| N55—C59A | 1.372 (6) | | |

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|---|---|---|---|
| C10A—S1—C2 | 91.7 (2) | C52—C53—C53A | 111.3 (4) |
| C12—O2—H2O | 113 (4) | C52—C53—C62 | 119.6 (5) |
| C9A—N5—C4 | 122.6 (4) | C53A—C53—C62 | 129.1 (4) |
| C9A—N5—C6 | 121.0 (4) | O51—C54—N55 | 118.9 (4) |
| C4—N5—C6 | 116.4 (4) | O51—C54—N55 | 118.9 (4) |
| C9A—N10—C10A | 115.4 (4) | O51—C54—C53A | 126.1 (5) |
| C3—C2—C11 | 130.6 (5) | O51—C54—C53A | 126.1 (5) |
| C3—C2—S1 | 112.8 (3) | N55—C54—C53A | 115.0 (4) |
| C11—C2—S1 | 116.6 (4) | C57—C56—N55 | 114 (2) |
| C2—C3—C3A | 111.1 (4) | C57—C56—H56A | 108.8 |
| C2—C3—C12 | 120.8 (4) | N55—C56—H56A | 108.8 |
| C3A—C3—C12 | 128.0 (4) | C57—C56—H56B | 108.8 |
| C10A—C3A—C4 | 116.4 (4) | N55—C56—H56B | 108.8 |
| C10A—C3A—C3 | 112.5 (4) | H56A—C56—H56B | 107.7 |
| C4—C3A—C3 | 131.0 (4) | C56—C57—C58 | 122 (3) |
| O1—C4—N5 | 118.8 (4) | C56—C57—H57A | 106.8 |
| O1—C4—N5 | 118.8 (4) | C58—C57—H57A | 106.8 |
| O1—C4—C3A | 126.0 (4) | C56—C57—H57B | 106.8 |
| O1—C4—C3A | 126.0 (4) | C58—C57—H57B | 106.8 |
| N5—C4—C3A | 115.2 (4) | H57A—C57—H57B | 106.6 |
| C7—C6—N5 | 118.0 (6) | C57—C58—C59 | 110.9 (19) |
| C7—C6—H6A | 107.8 | C57—C58—H58A | 109.5 |
| N5—C6—H6A | 107.8 | C59—C58—H58A | 109.5 |
| C7—C6—H6B | 107.8 | C57—C58—H58B | 109.5 |
| N5—C6—H6B | 107.8 | C59—C58—H58B | 109.5 |
| H6A—C6—H6B | 107.1 | H58A—C58—H58B | 108.0 |
| C6—C7—C8 | 120.6 (6) | C59A—C59—C58 | 117.1 (17) |
| C6—C7—H7A | 107.2 | C59A—C59—H59A | 108.0 |
| C8—C7—H7A | 107.2 | C58—C59—H59A | 108.0 |
| C6—C7—H7B | 107.2 | C59A—C59—H59B | 108.0 |
| C8—C7—H7B | 107.2 | C58—C59—H59B | 108.0 |
| H7A—C7—H7B | 106.8 | H59A—C59—H59B | 107.3 |
| C7—C8—C9 | 110.9 (5) | C57′—C56′—N55 | 116.8 (18) |
| C7—C8—H8A | 109.5 | C57′—C56′—H56C | 108.1 |
| C9—C8—H8A | 109.5 | N55—C56′—H56C | 108.1 |
| C7—C8—H8B | 109.5 | C57′—C56′—H56D | 108.1 |
| C9—C8—H8B | 109.5 | N55—C56′—H56D | 108.1 |
| H8A—C8—H8B | 108.1 | H56C—C56′—H56D | 107.3 |
| C9A—C9—C8 | 114.1 (5) | C56′—C57′—C58′ | 119 (2) |
| C9A—C9—H9A | 108.7 | C56′—C57′—H57C | 107.4 |
| C8—C9—H9A | 108.7 | C58′—C57′—H57C | 107.4 |
| C9A—C9—H9B | 108.7 | C56′—C57′—H57D | 107.4 |
| C8—C9—H9B | 108.7 | C58′—C57′—H57D | 107.5 |
| H9A—C9—H9B | 107.6 | H57C—C57′—H57D | 107.0 |
| N10—C9A—N5 | 123.2 (4) | C57′—C58′—C59′ | 108.7 (19) |
| N10—C9A—C9 | 118.6 (4) | C57′—C58′—H58C | 110.0 |
| N5—C9A—C9 | 118.2 (4) | C59′—C58′—H58C | 110.0 |
| N10—C10A—C3A | 127.2 (4) | C57′—C58′—H58D | 110.0 |

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|---|---|---|---|
| N10—C10A—S1 | 121.0 (3) | C59′—C58′—H58D | 110.0 |
| C3A—C10A—S1 | 111.8 (3) | H58C—C58′—H58D | 108.3 |
| C2—C11—H11A | 109.5 | C59A—C59′—C58′ | 110.1 (15) |
| C2—C11—H11B | 109.5 | C59A—C59′—H59C | 109.6 |
| H11A—C11—H11B | 109.5 | C58′—C59′—H59C | 109.6 |
| C2—C11—H11C | 109.5 | C59A—C59′—H59D | 109.6 |
| H11A—C11—H11C | 109.5 | C58′—C59′—H59D | 109.6 |
| H11B—C11—H11C | 109.5 | H59C—C59′—H59D | 108.2 |
| O3—C12—O2 | 118.8 (5) | N60—C59A—N55 | 122.8 (4) |
| O3—C12—C3 | 122.5 (5) | N60—C59A—C59 | 120.2 (10) |
| O2—C12—C3 | 118.7 (5) | N55—C59A—C59 | 117.0 (10) |
| C52—S51—C60A | 92.2 (2) | N60—C59A—C59′ | 115.4 (9) |
| C62—O52—H52O | 124 (3) | N55—C59A—C59′ | 121.9 (9) |
| C59A—N55—C54 | 122.7 (4) | N60—C60A—C53A | 126.6 (4) |
| C59A—N55—C56 | 124.9 (12) | N60—C60A—S51 | 121.8 (3) |
| C54—N55—C56 | 111.7 (12) | C53A—C60A—S51 | 111.6 (3) |
| C59A—N55—C56′ | 119.0 (10) | C52—C61—H61A | 109.5 |
| C54—N55—C56′ | 118.2 (10) | C52—C61—H61B | 109.5 |
| C59A—N60—C60A | 115.8 (4) | H61A—C61—H61B | 109.5 |
| C53—C52—C61 | 129.8 (5) | C52—C61—H61C | 109.5 |
| C53—C52—S51 | 112.4 (4) | H61A—C61—H61C | 109.5 |
| C61—C52—S51 | 117.8 (4) | H61B—C61—H61C | 109.5 |
| C60A—C53A—C54 | 117.1 (4) | O53—C62—O52 | 118.6 (6) |
| C60A—C53A—C53 | 112.4 (4) | O53—C62—C53 | 123.5 (6) |
| C54—C53A—C53 | 130.5 (4) | O52—C62—C53 | 117.9 (5) |

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|---|---|---|---|
| C10A—S1—C2—C3 | 0.1 (4) | C59A—N55—C54—O51 | −177.8 (4) |
| C10A—S1—C2—C11 | −178.4 (4) | C56—N55—C54—O51 | 11 (3) |
| C11—C2—C3—C3A | 178.0 (5) | C56′—N55—C54—O51 | −2 (2) |
| S1—C2—C3—C3A | −0.2 (5) | C59A—N55—C54—O51 | −177.8 (4) |
| C11—C2—C3—C12 | −2.1 (8) | C56—N55—C54—O51 | 11 (3) |
| S1—C2—C3—C12 | 179.7 (3) | C56′—N55—C54—O51 | −2 (2) |
| C2—C3—C3A—C10A | 0.3 (5) | C59A—N55—C54—C53A | 2.4 (6) |
| C12—C3—C3A—C10A | −179.6 (4) | C56—N55—C54—C53A | −169 (3) |
| C2—C3—C3A—C4 | −177.3 (4) | C56′—N55—C54—C53A | 178 (2) |
| C12—C3—C3A—C4 | 2.8 (8) | C60A—C53A—C54—O51 | 177.1 (5) |
| C9A—N5—C4—O1 | 177.0 (5) | C53—C53A—C54—O51 | −3.2 (8) |
| C6—N5—C4—O1 | −0.2 (8) | C60A—C53A—C54—O51 | 177.1 (5) |
| C9A—N5—C4—O1 | 177.0 (5) | C53—C53A—C54—O51 | −3.2 (8) |
| C6—N5—C4—O1 | −0.2 (8) | C60A—C53A—C54—N55 | −3.1 (6) |
| C9A—N5—C4—C3A | −2.2 (7) | C53—C53A—C54—N55 | 176.6 (4) |
| C6—N5—C4—C3A | −179.5 (5) | C59A—N55—C56—C57 | 3 (6) |
| C10A—C3A—C4—O1 | −176.9 (5) | C54—N55—C56—C57 | 174 (4) |
| C3—C3A—C4—O1 | 0.6 (8) | C56′—N55—C56—C57 | −65 (10) |
| C10A—C3A—C4—O1 | −176.9 (5) | N55—C56—C57—C58 | 25 (7) |
| C3—C3A—C4—O1 | 0.6 (8) | C56—C57—C58—C59 | −44 (6) |
| C10A—C3A—C4—N5 | 2.2 (6) | C57—C58—C59—C59A | 37 (5) |
| C3—C3A—C4—N5 | 179.7 (4) | C59A—N55—C56′—C57′ | −9 (5) |

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| C9A—N5—C6—C7 | 0.7 (11) | C54—N55—C56′—C57′ | 176 (3) |
| C4—N5—C6—C7 | 178.0 (8) | C56—N55—C56′—C57′ | 111 (15) |
| N5—C6—C7—C8 | −23.3 (14) | N55—C56′—C57′—C58′ | −20 (6) |
| C6—C7—C8—C9 | 45.4 (12) | C56′—C57′—C58′—C59′ | 52 (4) |
| C7—C8—C9—C9A | −45.3 (8) | C57′—C58′—C59′—C59A | −53 (4) |
| C10A—N10—C9A—N5 | −0.1 (7) | C60A—N60—C59A—N55 | −0.8 (7) |
| C10A—N10—C9A—C9 | −178.2 (5) | C60A—N60—C59A—C59 | 176 (3) |
| C4—N5—C9A—N10 | 1.2 (8) | C60A—N60—C59A—C59′ | −180 (2) |
| C6—N5—C9A—N10 | 178.3 (6) | C54—N55—C59A—N60 | −0.4 (7) |
| C4—N5—C9A—C9 | 179.4 (5) | C56—N55—C59A—N60 | 170 (3) |
| C6—N5—C9A—C9 | −3.6 (8) | C56′—N55—C59A—N60 | −176 (2) |
| C8—C9—C9A—N10 | −155.3 (5) | C54—N55—C59A—C59 | −177 (3) |
| C8—C9—C9A—N5 | 26.4 (8) | C56—N55—C59A—C59 | −7 (4) |
| C9A—N10—C10A—C3A | 0.2 (7) | C56′—N55—C59A—C59 | 7 (4) |
| C9A—N10—C10A—S1 | −178.8 (3) | C54—N55—C59A—C59′ | 179 (2) |
| C4—C3A—C10A—N10 | −1.3 (7) | C56—N55—C59A—C59′ | −11 (4) |
| C3—C3A—C10A—N10 | −179.3 (4) | C56′—N55—C59A—C59′ | 3 (3) |
| C4—C3A—C10A—S1 | 177.7 (3) | C58—C59—C59A—N60 | 169 (2) |
| C3—C3A—C10A—S1 | −0.2 (5) | C58—C59—C59A—N55 | −14 (5) |
| C2—S1—C10A—N10 | 179.2 (4) | C58—C59—C59A—C59′ | 131 (38) |
| C2—S1—C10A—C3A | 0.1 (3) | C58′—C59′—C59A—N60 | −152.3 (19) |
| C2—C3—C12—O3 | −3.2 (8) | C58′—C59′—C59A—N55 | 29 (4) |
| C3A—C3—C12—O3 | 176.6 (5) | C58′—C59′—C59A—C59 | −9 (33) |
| C2—C3—C12—O2 | 176.1 (5) | C59A—N60—C60A—C53A | −0.1 (7) |
| C3A—C3—C12—O2 | −4.0 (7) | C59A—N60—C60A—S51 | −178.3 (4) |
| C60A—S51—C52—C53 | 1.0 (4) | C54—C53A—C60A—N60 | 2.2 (7) |
| C60A—S51—C52—C61 | 179.9 (4) | C53—C53A—C60A—N60 | −177.5 (4) |
| C61—C52—C53—C53A | −179.5 (5) | C54—C53A—C60A—S51 | −179.5 (3) |
| S51—C52—C53—C53A | −0.7 (5) | C53—C53A—C60A—S51 | 0.8 (5) |
| C61—C52—C53—C62 | 1.5 (8) | C52—S51—C60A—N60 | 177.4 (4) |
| S51—C52—C53—C62 | −179.7 (4) | C52—S51—C60A—C53A | −1.0 (3) |
| C60A—C53A—C53—C52 | 0.0 (5) | C52—C53—C62—O53 | 4.9 (8) |
| C54—C53A—C53—C52 | −179.7 (4) | C53A—C53—C62—O53 | −173.9 (5) |
| C60A—C53A—C53—C62 | 178.8 (5) | C52—C53—C62—O52 | −172.6 (5) |
| C54—C53A—C53—C62 | −0.8 (8) | C53A—C53—C62—O52 | 8.6 (8) |

*Hydrogen-bond geometry (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| O2—H2*O*···O1 | 0.87 (2) | 1.63 (2) | 2.501 (5) | 177 (7) |
| O52—H52*O*···O51 | 0.87 (2) | 1.71 (3) | 2.518 (6) | 154 (4) |