# 2-[(E)-1,1-Dioxo-2-(2,4,5-trifluorobenzyl)-3,4-dihydro-2H-1,2-benzothiazin-4-ylidene]acetic acid

## Shaojuan Zhu, Shagufta Parveen and Changjin Zhu*

School of Chemical Engineering and Environment, Beijing Institute of Technology, Beijing 100081, People's Republic of China
Correspondence e-mail: zcj@bit.edu.cn

In the asymmetric unit of the title compound, $C_{17}H_{12}F_3NO_4S$, there are two conformationally similar molecules in which the heterocyclic thiazine ring adopts a half-chair conformation, with the dihedral angle between the two benzene rings being 24.84 (8) and 37.42 (8)°. In the crystal, the molecules form dimers through cyclic carboxylic acid O—H⋯O hydrogen-bonding associations [graph set $R_2^2(8)$] and are extended into chains along [101] through weak C—H⋯O$_{sulfinyl}$ hydrogen bonds [graph set $R_2^2(14)$]..

## Related literature

For pharmaceutical and biological properties of 1,2-benzothiazines, see: Zia-ur-Rehman et al. (2005); Lombardino et al. (1971); Bihovsky et al. (2004); For synthetic details of the title compound, see: Parveen et al. (2014b). For related structures, see: Yang et al. (2012); Parveen et al. (2014a). For graph-set analysis, see: Etter et al. 1990).
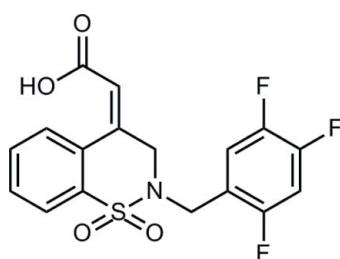


## Experimental

### Crystal data

$C_{17}H_{12}F_3NO_4S$
$M_r = 383.34$
Triclinic, $P\bar{1}$
$a = 8.0028$ (10) Å
$b = 14.249$ (2) Å
$c = 15.076$ (2) Å
$\alpha = 104.631$ (8)°
$\beta = 99.915$ (6)°
$\gamma = 104.237$ (6)°
$V = 1561.2$ (4) Å$^3$
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 0.27$ mm$^{-1}$
$T = 153$ K
$0.31 \times 0.26 \times 0.18$ mm

### Data collection

Rigaku AFC10/Saturn724+ CCD-detector diffractometer
Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2008)
$T_{min} = 0.932$, $T_{max} = 0.964$
20894 measured reflections
8293 independent reflections
6954 reflections with $I > 2\sigma(I)$
$R_{int} = 0.030$

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.042$
$wR(F^2) = 0.114$
$S = 1.00$
8293 reflections
477 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max} = 0.32$ e Å$^{-3}$
$\Delta\rho_{min} = -0.43$ e Å$^{-3}$

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

| $D$—H⋯$A$ | $D$—H | H⋯$A$ | $D$⋯$A$ | $D$—H⋯$A$ |
|---|---|---|---|---|
| O3—H3$O$⋯O8$^i$ | 0.85 (3) | 1.86 (3) | 2.7063 (17) | 172 (3) |
| O7—H7$O$⋯O4$^{ii}$ | 0.92 (3) | 1.73 (3) | 2.6473 (17) | 177 (2) |
| C15—H15⋯O6 | 0.95 | 2.34 | 3.267 (2) | 165 |
| C32—H32⋯O2 | 0.95 | 2.61 | 3.539 (2) | 165 |

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

Data collection: *CrystalClear* (Rigaku, 2008); cell refinement: *CrystalClear* (Rigaku, 2008); data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 1998); software used to prepare material for publication: *CrystalStructure* (Rigaku, 2008).

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# supporting information

## 2-[(*E*)-1,1-Dioxo-2-(2,4,5-trifluorobenzyl)-3,4-dihydro-2*H*-1,2-benzothiazin-4-ylidene]acetic acid

**Shaojuan Zhu, Shagufta Parveen and Changjin Zhu**

### S1. Comment

1,2-Benzothiazine-1,1-dioxide derivatives are reported as having anti- inflammatory and anti-bacterial activities (Lombardino *et al.*, 1971) while some of its derivatives have been found to be calpain 1 inhibitors (Bihovsky *et al.*, 2004). More recently, its derivatives were reported as aldose reductase inhibitors (Parveen *et al.*, 2014*b*). Herein, we report the structure of the title derivative, $C_{17}H_{12}F_3NO_4S$, which is the *E* isomer of the previously published isomer 2-[(*Z*)-1,1-dioxo-2-(2,4,5-trifluorobenzyl)-3,4- dihydro-2*H*-1,2-benzothiazin-4-ylidene]acetic acid (Parveen *et al.*, 2014*a*).

In the title compound, there are two conformationally similar molecules (*A* and *B*) in the asymmetric unit (Fig. 1). The dihedral angles between mean plane of the two benzene rings [(C1—C6) and (C10—C15) in *A* and (C18–C23) and (C27–C32) in *B*] are 37.42 (8) and 24.84 (7)°, respectively. These values compare with 43.28 (9)° in the *Z* isomer (Parveen *et al.*, 2014*a*). The heterocyclic thiazine ring adopts a half-chair conformation. The acetic acid substituent groups show only minor conformational differences: torsion angles C8—C7—C16—C17 and C7—C16—C17—O3 [169.7 (16) and 174.59 (17)°, respectively] in *A* campare with C25—C24— C33—C34 and C24—C33—C34—O7 [-179.25 (16) and -168.18 (17), respectively] in *B*.

In the crystal the molecules form centrosymmetric dimers through intermolecular cyclic carboxylic acid O—H···O hydrogen-bonding associations [graph set $R_2^2(8)$ (Etter *et al.*, 1990)]. These dimers form one-dimensional chains which extend along [101] (Fig. 2), through weak duplex C—H···O$_{sulfinyl}$ hydrogen-bonding associations (Table 1) [graph set $R_2^2(14)$].

### S2. Experimental

A mixture of *E*-2-[2-(2,4,5-Trifluorobenzyl)-1,1-dioxido-2*H*-1,2-benzothiazin- 4(3*H*)-ylidene]acetic acid methyl ester (0.5 mmol), 10 *M* hydrochloric acid (8 mL), and 1,4-dioxane (5 mL) was refluxed at 60°C for 2 h. The crude product obtained was washed with cold water (3 times, 10 mL) and purified by flash chromatography with $CH_2Cl_2$ and methanol (100:1) as eluent, which afforded a white solid product on concentration under vacuum. Recrystallization from ethanol gave crystals of the title compound suitable for the X-ray analysis (yield = 60%).

### S3. Refinement

H atoms bonded to O1 and O3 were located from a difference-Fourier map and were refined freely. The remaining H atoms were positioned geometrically, with C—H = 0.95 and 0.99 Å for aromatic and methylene H, respectively, and constrained to ride on their parent atoms with $U_{iso}(H) = 1.2U_{eq}(C)$.
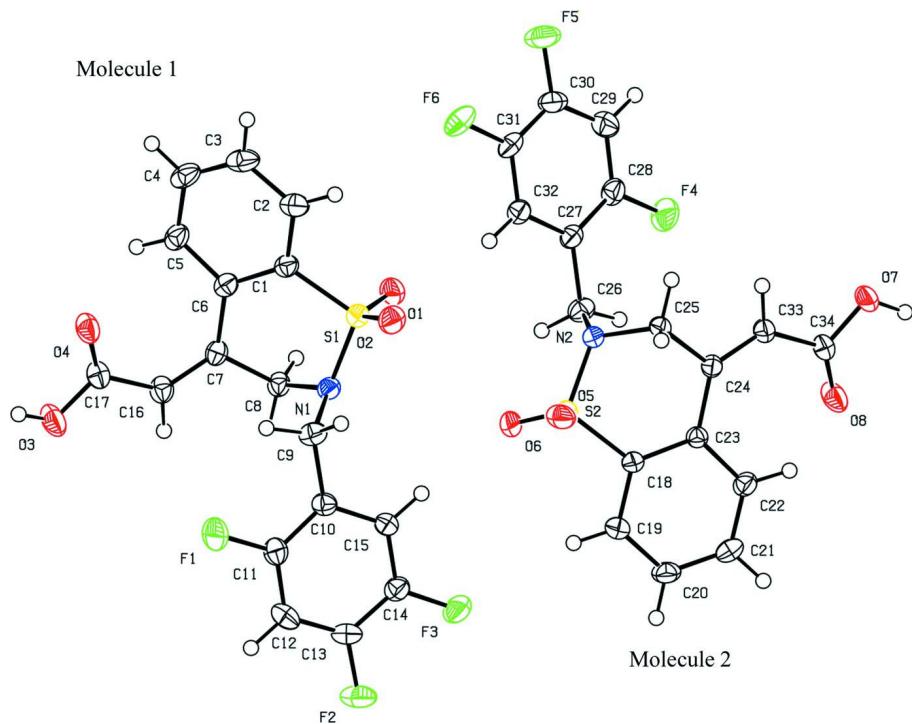
**Figure 1**

The molecular conformation and atom numbering scheme for the two independent molecules (*A* and *B*) of the title compound in the asymmetric unit. Displacement ellipsoids are drawn at the 50% probability level.
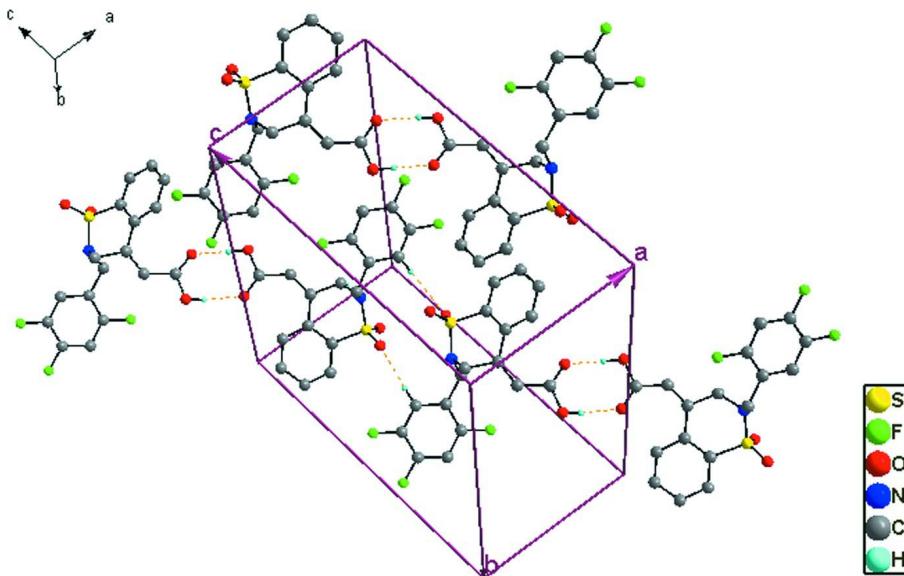


**Figure 2**

Hydrogen-bonding interactions (O—H···O and C—H···O), shown as dashed lines, in the one-dimensional chain structure of the title compound. H atoms non–participating in hydrogen-bonding are omitted for clarity.

**2-[(*E*)-1,1-Dioxo-2-(2,4,5-trifluorobenzyl)-3,4-dihydro-2*H*-1,2-benzothiazin-4-ylidene]acetic acid**

*Crystal data*

| | |
|---|---|
| $C_{17}H_{12}F_3NO_4S$ | $Z = 4$ |
| $M_r = 383.34$ | $F(000) = 784$ |
| Triclinic, $P\overline{1}$ | $D_x = 1.631$ Mg m$^{-3}$ |
| $a = 8.0028$ (10) Å | Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å |
| $b = 14.249$ (2) Å | Cell parameters from 5221 reflections |
| $c = 15.076$ (2) Å | $\theta = 2.4$–29.1° |
| $\alpha = 104.631$ (8)° | $\mu = 0.27$ mm$^{-1}$ |
| $\beta = 99.915$ (6)° | $T = 153$ K |
| $\gamma = 104.237$ (6)° | Prism, colourless |
| $V = 1561.2$ (4) Å$^3$ | 0.31 × 0.26 × 0.18 mm |

*Data collection*

| | |
|---|---|
| Rigaku AFC10/Saturn724+ CCD-detector diffractometer | 20894 measured reflections |
| | 8293 independent reflections |
| Radiation source: Rotating Anode | 6954 reflections with $I > 2\sigma(I)$ |
| Graphite monochromator | $R_{int} = 0.030$ |
| Detector resolution: 28.5714 pixels mm$^{-1}$ | $\theta_{max} = 29.1°$, $\theta_{min} = 2.7°$ |
| $\varphi$ and $\omega$ scans | $h = -10 \rightarrow 10$ |
| Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2008) | $k = -19 \rightarrow 19$ |
| | $l = -20 \rightarrow 20$ |
| $T_{min} = 0.932$, $T_{max} = 0.964$ | |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | Secondary atom site location: difference Fourier map |
| Least-squares matrix: full | |
| $R[F^2 > 2\sigma(F^2)] = 0.042$ | Hydrogen site location: inferred from neighbouring sites |
| $wR(F^2) = 0.114$ | |
| $S = 1.00$ | H atoms treated by a mixture of independent and constrained refinement |
| 8293 reflections | |
| 477 parameters | $w = 1/[\sigma^2(F_o^2) + (0.061P)^2 + 0.226P]$ where $P = (F_o^2 + 2F_c^2)/3$ |
| 0 restraints | |
| Primary atom site location: structure-invariant direct methods | $(\Delta/\sigma)_{max} = 0.001$ |
| | $\Delta\rho_{max} = 0.32$ e Å$^{-3}$ |
| | $\Delta\rho_{min} = -0.43$ e Å$^{-3}$ |

*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 (Å$^2$)*

| | $x$ | $y$ | $z$ | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| S1 | 0.73455 (5) | 0.69761 (3) | 0.55702 (3) | 0.02391 (10) |
| S2 | 0.50292 (5) | 0.87262 (3) | 0.79867 (3) | 0.02531 (10) |
| F1 | 0.58349 (14) | 0.89772 (9) | 0.31143 (8) | 0.0450 (3) |

| | | | |
|---|---|---|---|
| F2 | 0.03716 (14) | 0.93851 (8) | 0.35868 (8) | 0.0423 (3) |
| F3 | 0.08711 (14) | 0.88184 (8) | 0.51527 (8) | 0.0391 (3) |
| F4 | 0.45408 (14) | 0.54711 (9) | 0.91587 (8) | 0.0431 (3) |
| F5 | 1.01396 (15) | 0.50243 (9) | 0.90295 (8) | 0.0469 (3) |
| F6 | 1.06588 (13) | 0.63243 (8) | 0.80223 (8) | 0.0387 (3) |
| O1 | 0.63170 (15) | 0.60907 (9) | 0.57395 (8) | 0.0311 (3) |
| O2 | 0.82039 (16) | 0.78775 (9) | 0.63550 (8) | 0.0328 (3) |
| O4 | 0.99668 (15) | 0.69914 (10) | 0.24217 (8) | 0.0337 (3) |
| O3 | 0.78052 (17) | 0.70022 (12) | 0.12780 (9) | 0.0417 (3) |
| O5 | 0.63875 (15) | 0.96931 (9) | 0.83329 (9) | 0.0335 (3) |
| O6 | 0.44968 (17) | 0.82015 (11) | 0.69925 (8) | 0.0386 (3) |
| O7 | 0.26182 (16) | 0.72184 (10) | 1.15812 (9) | 0.0334 (3) |
| O8 | 0.06107 (15) | 0.74619 (10) | 1.05181 (9) | 0.0379 (3) |
| N1 | 0.60349 (16) | 0.72401 (9) | 0.47719 (9) | 0.0224 (3) |
| N2 | 0.56830 (16) | 0.79812 (10) | 0.85392 (9) | 0.0232 (3) |
| C1 | 0.89250 (19) | 0.65910 (11) | 0.49927 (11) | 0.0233 (3) |
| C2 | 1.0447 (2) | 0.65398 (12) | 0.55604 (13) | 0.0298 (3) |
| H2 | 1.0695 | 0.6801 | 0.6230 | 0.036* |
| C3 | 1.1599 (2) | 0.61036 (13) | 0.51375 (14) | 0.0344 (4) |
| H3 | 1.2670 | 0.6092 | 0.5515 | 0.041* |
| C4 | 1.1179 (2) | 0.56859 (13) | 0.41639 (14) | 0.0341 (4) |
| H4 | 1.1912 | 0.5334 | 0.3879 | 0.041* |
| C5 | 0.9703 (2) | 0.57747 (12) | 0.35992 (13) | 0.0286 (3) |
| H5 | 0.9452 | 0.5495 | 0.2931 | 0.034* |
| C6 | 0.85747 (19) | 0.62700 (11) | 0.39983 (11) | 0.0234 (3) |
| C7 | 0.70501 (19) | 0.64394 (11) | 0.34115 (11) | 0.0232 (3) |
| C8 | 0.54758 (19) | 0.64252 (11) | 0.38476 (11) | 0.0238 (3) |
| H8A | 0.4509 | 0.6533 | 0.3417 | 0.029* |
| H8B | 0.5017 | 0.5755 | 0.3940 | 0.029* |
| C9 | 0.6528 (2) | 0.82967 (12) | 0.47205 (12) | 0.0273 (3) |
| H9A | 0.7281 | 0.8352 | 0.4268 | 0.033* |
| H9B | 0.7224 | 0.8774 | 0.5350 | 0.033* |
| C10 | 0.4876 (2) | 0.85800 (11) | 0.44047 (11) | 0.0237 (3) |
| C11 | 0.4596 (2) | 0.89144 (12) | 0.36246 (12) | 0.0291 (3) |
| C12 | 0.3112 (2) | 0.91996 (13) | 0.33337 (12) | 0.0320 (4) |
| H12 | 0.2965 | 0.9430 | 0.2795 | 0.038* |
| C13 | 0.1865 (2) | 0.91365 (12) | 0.38516 (12) | 0.0285 (3) |
| C14 | 0.2105 (2) | 0.88278 (12) | 0.46446 (12) | 0.0266 (3) |
| C15 | 0.3584 (2) | 0.85423 (11) | 0.49217 (11) | 0.0245 (3) |
| H15 | 0.3727 | 0.8319 | 0.5465 | 0.029* |
| C16 | 0.6974 (2) | 0.66706 (12) | 0.25983 (11) | 0.0274 (3) |
| H16 | 0.5849 | 0.6697 | 0.2297 | 0.033* |
| C17 | 0.8406 (2) | 0.68902 (12) | 0.21090 (11) | 0.0273 (3) |
| C18 | 0.31608 (19) | 0.89025 (11) | 0.83939 (11) | 0.0224 (3) |
| C19 | 0.2095 (2) | 0.93054 (13) | 0.78660 (12) | 0.0291 (3) |
| H19 | 0.2374 | 0.9444 | 0.7315 | 0.035* |
| C20 | 0.0627 (2) | 0.95032 (13) | 0.81459 (12) | 0.0304 (3) |
| H20 | −0.0118 | 0.9772 | 0.7787 | 0.036* |

| | | | | |
|---|---|---|---|---|
| C21 | 0.0259 (2) | 0.93060 (12) | 0.89503 (12) | 0.0282 (3) |
| H21 | −0.0744 | 0.9447 | 0.9147 | 0.034* |
| C22 | 0.1323 (2) | 0.89045 (11) | 0.94806 (11) | 0.0257 (3) |
| H22 | 0.1043 | 0.8787 | 1.0038 | 0.031* |
| C23 | 0.27989 (18) | 0.86690 (10) | 0.92127 (10) | 0.0199 (3) |
| C24 | 0.39674 (19) | 0.82390 (11) | 0.97612 (10) | 0.0207 (3) |
| C25 | 0.57919 (19) | 0.83583 (12) | 0.95578 (10) | 0.0225 (3) |
| H25A | 0.6501 | 0.9087 | 0.9807 | 0.027* |
| H25B | 0.6418 | 0.7981 | 0.9894 | 0.027* |
| C26 | 0.4900 (2) | 0.68674 (12) | 0.80941 (12) | 0.0276 (3) |
| H26A | 0.4519 | 0.6705 | 0.7398 | 0.033* |
| H26B | 0.3843 | 0.6616 | 0.8324 | 0.033* |
| C27 | 0.6278 (2) | 0.63582 (11) | 0.83449 (11) | 0.0237 (3) |
| C28 | 0.6062 (2) | 0.56868 (12) | 0.88642 (12) | 0.0286 (3) |
| C29 | 0.7309 (2) | 0.52137 (13) | 0.91045 (13) | 0.0346 (4) |
| H29 | 0.7113 | 0.4752 | 0.9461 | 0.042* |
| C30 | 0.8843 (2) | 0.54411 (13) | 0.88054 (12) | 0.0316 (4) |
| C31 | 0.9114 (2) | 0.61120 (12) | 0.82925 (11) | 0.0266 (3) |
| C32 | 0.7862 (2) | 0.65739 (11) | 0.80590 (11) | 0.0249 (3) |
| H32 | 0.8071 | 0.7037 | 0.7705 | 0.030* |
| C33 | 0.3679 (2) | 0.77728 (11) | 1.04221 (11) | 0.0242 (3) |
| H33 | 0.4672 | 0.7587 | 1.0681 | 0.029* |
| C34 | 0.2146 (2) | 0.74921 (11) | 1.08260 (11) | 0.0250 (3) |
| H7O | 0.168 (3) | 0.7121 (19) | 1.1855 (17) | 0.067 (8)* |
| H3O | 0.865 (4) | 0.720 (2) | 0.1031 (19) | 0.077 (9)* |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| S1 | 0.02321 (19) | 0.02732 (19) | 0.0232 (2) | 0.00954 (14) | 0.00707 (15) | 0.00851 (14) |
| S2 | 0.02388 (19) | 0.0386 (2) | 0.0241 (2) | 0.01631 (16) | 0.01081 (15) | 0.01787 (16) |
| F1 | 0.0420 (6) | 0.0616 (7) | 0.0486 (7) | 0.0182 (5) | 0.0274 (5) | 0.0332 (6) |
| F2 | 0.0334 (6) | 0.0458 (6) | 0.0555 (7) | 0.0206 (5) | 0.0046 (5) | 0.0252 (5) |
| F3 | 0.0347 (5) | 0.0464 (6) | 0.0510 (7) | 0.0214 (5) | 0.0237 (5) | 0.0229 (5) |
| F4 | 0.0389 (6) | 0.0487 (6) | 0.0551 (7) | 0.0143 (5) | 0.0289 (5) | 0.0267 (5) |
| F5 | 0.0471 (7) | 0.0532 (7) | 0.0505 (7) | 0.0352 (6) | 0.0067 (5) | 0.0174 (6) |
| F6 | 0.0234 (5) | 0.0409 (6) | 0.0516 (7) | 0.0125 (4) | 0.0154 (5) | 0.0070 (5) |
| O1 | 0.0305 (6) | 0.0368 (6) | 0.0326 (6) | 0.0106 (5) | 0.0128 (5) | 0.0184 (5) |
| O2 | 0.0334 (6) | 0.0353 (6) | 0.0253 (6) | 0.0123 (5) | 0.0042 (5) | 0.0023 (5) |
| O4 | 0.0260 (6) | 0.0490 (7) | 0.0280 (6) | 0.0065 (5) | 0.0093 (5) | 0.0182 (5) |
| O3 | 0.0297 (7) | 0.0699 (10) | 0.0330 (7) | 0.0114 (6) | 0.0110 (5) | 0.0304 (7) |
| O5 | 0.0253 (6) | 0.0410 (7) | 0.0467 (8) | 0.0122 (5) | 0.0143 (5) | 0.0293 (6) |
| O6 | 0.0427 (7) | 0.0659 (9) | 0.0222 (6) | 0.0336 (7) | 0.0137 (5) | 0.0188 (6) |
| O7 | 0.0327 (6) | 0.0492 (7) | 0.0321 (7) | 0.0171 (6) | 0.0153 (5) | 0.0269 (6) |
| O8 | 0.0249 (6) | 0.0608 (8) | 0.0334 (7) | 0.0077 (6) | 0.0080 (5) | 0.0283 (6) |
| N1 | 0.0209 (6) | 0.0236 (6) | 0.0241 (6) | 0.0081 (5) | 0.0066 (5) | 0.0075 (5) |
| N2 | 0.0228 (6) | 0.0309 (7) | 0.0217 (6) | 0.0132 (5) | 0.0079 (5) | 0.0112 (5) |
| C1 | 0.0214 (7) | 0.0221 (7) | 0.0293 (8) | 0.0075 (5) | 0.0089 (6) | 0.0104 (6) |

| | | | | | |
|---|---|---|---|---|---|
| C2 | 0.0246 (8) | 0.0301 (8) | 0.0381 (9) | 0.0092 (6) | 0.0062 (7) | 0.0166 (7) |
| C3 | 0.0222 (8) | 0.0323 (8) | 0.0563 (12) | 0.0104 (7) | 0.0107 (8) | 0.0239 (8) |
| C4 | 0.0278 (8) | 0.0303 (8) | 0.0588 (12) | 0.0144 (7) | 0.0246 (8) | 0.0240 (8) |
| C5 | 0.0290 (8) | 0.0259 (7) | 0.0379 (9) | 0.0102 (6) | 0.0182 (7) | 0.0136 (7) |
| C6 | 0.0215 (7) | 0.0198 (6) | 0.0310 (8) | 0.0056 (5) | 0.0105 (6) | 0.0094 (6) |
| C7 | 0.0211 (7) | 0.0229 (7) | 0.0237 (7) | 0.0047 (5) | 0.0073 (6) | 0.0050 (6) |
| C8 | 0.0208 (7) | 0.0268 (7) | 0.0237 (8) | 0.0063 (6) | 0.0070 (6) | 0.0076 (6) |
| C9 | 0.0226 (7) | 0.0239 (7) | 0.0368 (9) | 0.0076 (6) | 0.0074 (6) | 0.0109 (6) |
| C10 | 0.0236 (7) | 0.0205 (7) | 0.0272 (8) | 0.0060 (6) | 0.0058 (6) | 0.0088 (6) |
| C11 | 0.0287 (8) | 0.0303 (8) | 0.0325 (9) | 0.0071 (6) | 0.0133 (7) | 0.0148 (7) |
| C12 | 0.0360 (9) | 0.0315 (8) | 0.0309 (9) | 0.0082 (7) | 0.0050 (7) | 0.0180 (7) |
| C13 | 0.0249 (8) | 0.0239 (7) | 0.0367 (9) | 0.0096 (6) | 0.0013 (7) | 0.0115 (6) |
| C14 | 0.0253 (7) | 0.0252 (7) | 0.0318 (9) | 0.0089 (6) | 0.0104 (6) | 0.0100 (6) |
| C15 | 0.0273 (8) | 0.0247 (7) | 0.0255 (8) | 0.0100 (6) | 0.0079 (6) | 0.0115 (6) |
| C16 | 0.0232 (7) | 0.0315 (8) | 0.0257 (8) | 0.0049 (6) | 0.0068 (6) | 0.0085 (6) |
| C17 | 0.0278 (8) | 0.0293 (8) | 0.0235 (8) | 0.0048 (6) | 0.0073 (6) | 0.0091 (6) |
| C18 | 0.0208 (7) | 0.0274 (7) | 0.0230 (7) | 0.0107 (6) | 0.0068 (6) | 0.0105 (6) |
| C19 | 0.0292 (8) | 0.0383 (9) | 0.0268 (8) | 0.0171 (7) | 0.0073 (6) | 0.0153 (7) |
| C20 | 0.0257 (8) | 0.0353 (8) | 0.0329 (9) | 0.0160 (7) | 0.0028 (7) | 0.0117 (7) |
| C21 | 0.0200 (7) | 0.0288 (8) | 0.0360 (9) | 0.0102 (6) | 0.0077 (6) | 0.0073 (7) |
| C22 | 0.0247 (7) | 0.0261 (7) | 0.0307 (8) | 0.0099 (6) | 0.0119 (6) | 0.0107 (6) |
| C23 | 0.0191 (7) | 0.0207 (6) | 0.0205 (7) | 0.0062 (5) | 0.0048 (5) | 0.0071 (5) |
| C24 | 0.0205 (7) | 0.0223 (7) | 0.0197 (7) | 0.0065 (5) | 0.0060 (5) | 0.0063 (5) |
| C25 | 0.0209 (7) | 0.0293 (7) | 0.0214 (7) | 0.0105 (6) | 0.0059 (6) | 0.0117 (6) |
| C26 | 0.0208 (7) | 0.0298 (8) | 0.0302 (8) | 0.0085 (6) | 0.0042 (6) | 0.0065 (6) |
| C27 | 0.0213 (7) | 0.0260 (7) | 0.0234 (8) | 0.0086 (6) | 0.0063 (6) | 0.0050 (6) |
| C28 | 0.0273 (8) | 0.0301 (8) | 0.0313 (9) | 0.0090 (6) | 0.0135 (7) | 0.0101 (6) |
| C29 | 0.0439 (10) | 0.0333 (9) | 0.0340 (9) | 0.0171 (8) | 0.0124 (8) | 0.0162 (7) |
| C30 | 0.0331 (9) | 0.0328 (8) | 0.0307 (9) | 0.0194 (7) | 0.0021 (7) | 0.0075 (7) |
| C31 | 0.0196 (7) | 0.0283 (8) | 0.0293 (8) | 0.0093 (6) | 0.0075 (6) | 0.0019 (6) |
| C32 | 0.0244 (7) | 0.0254 (7) | 0.0260 (8) | 0.0084 (6) | 0.0086 (6) | 0.0077 (6) |
| C33 | 0.0240 (7) | 0.0288 (7) | 0.0228 (7) | 0.0089 (6) | 0.0080 (6) | 0.0106 (6) |
| C34 | 0.0282 (8) | 0.0263 (7) | 0.0219 (7) | 0.0067 (6) | 0.0080 (6) | 0.0102 (6) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| S1—O2 | 1.4282 (12) | C9—H9A | 0.9900 |
| S1—O1 | 1.4347 (12) | C9—H9B | 0.9900 |
| S1—N1 | 1.6365 (13) | C10—C11 | 1.380 (2) |
| S1—C1 | 1.7708 (16) | C10—C15 | 1.396 (2) |
| S2—O6 | 1.4298 (13) | C11—C12 | 1.384 (2) |
| S2—O5 | 1.4342 (13) | C12—C13 | 1.369 (2) |
| S2—N2 | 1.6322 (13) | C12—H12 | 0.9500 |
| S2—C18 | 1.7603 (15) | C13—C14 | 1.374 (2) |
| F1—C11 | 1.3553 (18) | C14—C15 | 1.376 (2) |
| F2—C13 | 1.3525 (18) | C15—H15 | 0.9500 |
| F3—C14 | 1.3494 (18) | C16—C17 | 1.478 (2) |
| F4—C28 | 1.3578 (18) | C16—H16 | 0.9500 |

| | | | |
|---|---|---|---|
| F5—C30 | 1.3519 (19) | C18—C19 | 1.388 (2) |
| F6—C31 | 1.3554 (17) | C18—C23 | 1.415 (2) |
| O4—C17 | 1.2156 (19) | C19—C20 | 1.383 (2) |
| O3—C17 | 1.326 (2) | C19—H19 | 0.9500 |
| O3—H3O | 0.85 (3) | C20—C21 | 1.375 (2) |
| O7—C34 | 1.3189 (19) | C20—H20 | 0.9500 |
| O7—H7O | 0.92 (3) | C21—C22 | 1.389 (2) |
| O8—C34 | 1.2224 (19) | C21—H21 | 0.9500 |
| N1—C8 | 1.4841 (19) | C22—C23 | 1.401 (2) |
| N1—C9 | 1.4853 (19) | C22—H22 | 0.9500 |
| N2—C25 | 1.4725 (19) | C23—C24 | 1.485 (2) |
| N2—C26 | 1.480 (2) | C24—C33 | 1.351 (2) |
| C1—C2 | 1.392 (2) | C24—C25 | 1.521 (2) |
| C1—C6 | 1.407 (2) | C25—H25A | 0.9900 |
| C2—C3 | 1.388 (2) | C25—H25B | 0.9900 |
| C2—H2 | 0.9500 | C26—C27 | 1.508 (2) |
| C3—C4 | 1.383 (3) | C26—H26A | 0.9900 |
| C3—H3 | 0.9500 | C26—H26B | 0.9900 |
| C4—C5 | 1.385 (2) | C27—C28 | 1.379 (2) |
| C4—H4 | 0.9500 | C27—C32 | 1.397 (2) |
| C5—C6 | 1.401 (2) | C28—C29 | 1.383 (2) |
| C5—H5 | 0.9500 | C29—C30 | 1.373 (2) |
| C6—C7 | 1.487 (2) | C29—H29 | 0.9500 |
| C7—C16 | 1.343 (2) | C30—C31 | 1.374 (2) |
| C7—C8 | 1.516 (2) | C31—C32 | 1.372 (2) |
| C8—H8A | 0.9900 | C32—H32 | 0.9500 |
| C8—H8B | 0.9900 | C33—C34 | 1.475 (2) |
| C9—C10 | 1.510 (2) | C33—H33 | 0.9500 |
| | | | |
| O2—S1—O1 | 118.55 (7) | C13—C14—C15 | 120.66 (15) |
| O2—S1—N1 | 108.96 (7) | C14—C15—C10 | 120.07 (14) |
| O1—S1—N1 | 107.34 (7) | C14—C15—H15 | 120.0 |
| O2—S1—C1 | 110.39 (7) | C10—C15—H15 | 120.0 |
| O1—S1—C1 | 106.24 (7) | C7—C16—C17 | 128.74 (15) |
| N1—S1—C1 | 104.43 (7) | C7—C16—H16 | 115.6 |
| O6—S2—O5 | 118.94 (8) | C17—C16—H16 | 115.6 |
| O6—S2—N2 | 108.52 (7) | O4—C17—O3 | 122.46 (15) |
| O5—S2—N2 | 107.54 (7) | O4—C17—C16 | 125.63 (15) |
| O6—S2—C18 | 109.72 (7) | O3—C17—C16 | 111.87 (14) |
| O5—S2—C18 | 107.20 (7) | C19—C18—C23 | 122.65 (14) |
| N2—S2—C18 | 103.89 (7) | C19—C18—S2 | 115.21 (12) |
| C17—O3—H3O | 111.3 (19) | C23—C18—S2 | 122.13 (11) |
| C34—O7—H7O | 108.4 (16) | C20—C19—C18 | 119.63 (15) |
| C8—N1—C9 | 115.31 (12) | C20—C19—H19 | 120.2 |
| C8—N1—S1 | 111.40 (10) | C18—C19—H19 | 120.2 |
| C9—N1—S1 | 117.72 (10) | C21—C20—C19 | 119.25 (15) |
| C25—N2—C26 | 115.52 (12) | C21—C20—H20 | 120.4 |
| C25—N2—S2 | 110.86 (10) | C19—C20—H20 | 120.4 |

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|---|---|---|---|
| C26—N2—S2 | 118.25 (10) | C20—C21—C22 | 121.26 (15) |
| C2—C1—C6 | 121.78 (14) | C20—C21—H21 | 119.4 |
| C2—C1—S1 | 117.04 (12) | C22—C21—H21 | 119.4 |
| C6—C1—S1 | 120.96 (11) | C21—C22—C23 | 121.56 (15) |
| C3—C2—C1 | 119.30 (17) | C21—C22—H22 | 119.2 |
| C3—C2—H2 | 120.3 | C23—C22—H22 | 119.2 |
| C1—C2—H2 | 120.3 | C22—C23—C18 | 115.61 (14) |
| C4—C3—C2 | 119.67 (16) | C22—C23—C24 | 123.11 (13) |
| C4—C3—H3 | 120.2 | C18—C23—C24 | 121.24 (13) |
| C2—C3—H3 | 120.2 | C33—C24—C23 | 130.34 (14) |
| C3—C4—C5 | 120.76 (16) | C33—C24—C25 | 114.86 (13) |
| C3—C4—H4 | 119.6 | C23—C24—C25 | 114.79 (12) |
| C5—C4—H4 | 119.6 | N2—C25—C24 | 112.43 (12) |
| C4—C5—C6 | 121.02 (16) | N2—C25—H25A | 109.1 |
| C4—C5—H5 | 119.5 | C24—C25—H25A | 109.1 |
| C6—C5—H5 | 119.5 | N2—C25—H25B | 109.1 |
| C5—C6—C1 | 116.90 (15) | C24—C25—H25B | 109.1 |
| C5—C6—C7 | 122.38 (15) | H25A—C25—H25B | 107.8 |
| C1—C6—C7 | 120.71 (13) | N2—C26—C27 | 108.89 (12) |
| C16—C7—C6 | 127.74 (14) | N2—C26—H26A | 109.9 |
| C16—C7—C8 | 117.96 (14) | C27—C26—H26A | 109.9 |
| C6—C7—C8 | 114.11 (13) | N2—C26—H26B | 109.9 |
| N1—C8—C7 | 109.66 (12) | C27—C26—H26B | 109.9 |
| N1—C8—H8A | 109.7 | H26A—C26—H26B | 108.3 |
| C7—C8—H8A | 109.7 | C28—C27—C32 | 117.47 (14) |
| N1—C8—H8B | 109.7 | C28—C27—C26 | 122.76 (14) |
| C7—C8—H8B | 109.7 | C32—C27—C26 | 119.77 (14) |
| H8A—C8—H8B | 108.2 | F4—C28—C27 | 118.67 (14) |
| N1—C9—C10 | 110.27 (12) | F4—C28—C29 | 117.60 (15) |
| N1—C9—H9A | 109.6 | C27—C28—C29 | 123.74 (15) |
| C10—C9—H9A | 109.6 | C30—C29—C28 | 117.02 (16) |
| N1—C9—H9B | 109.6 | C30—C29—H29 | 121.5 |
| C10—C9—H9B | 109.6 | C28—C29—H29 | 121.5 |
| H9A—C9—H9B | 108.1 | F5—C30—C29 | 120.43 (16) |
| C11—C10—C15 | 117.22 (14) | F5—C30—C31 | 118.55 (16) |
| C11—C10—C9 | 122.38 (14) | C29—C30—C31 | 121.00 (15) |
| C15—C10—C9 | 120.36 (14) | F6—C31—C32 | 119.75 (15) |
| F1—C11—C10 | 118.92 (15) | F6—C31—C30 | 119.01 (14) |
| F1—C11—C12 | 117.63 (14) | C32—C31—C30 | 121.24 (15) |
| C10—C11—C12 | 123.44 (15) | C31—C32—C27 | 119.54 (15) |
| C13—C12—C11 | 117.47 (15) | C31—C32—H32 | 120.2 |
| C13—C12—H12 | 121.3 | C27—C32—H32 | 120.2 |
| C11—C12—H12 | 121.3 | C24—C33—C34 | 133.41 (15) |
| F2—C13—C12 | 119.91 (15) | C24—C33—H33 | 113.3 |
| F2—C13—C14 | 118.98 (15) | C34—C33—H33 | 113.3 |
| C12—C13—C14 | 121.11 (15) | O8—C34—O7 | 121.92 (14) |
| F3—C14—C13 | 118.81 (14) | O8—C34—C33 | 127.55 (14) |
| F3—C14—C15 | 120.53 (14) | O7—C34—C33 | 110.48 (14) |

| | | | |
|---|---|---|---|
| O2—S1—N1—C8 | 165.08 (10) | C11—C10—C15—C14 | 0.3 (2) |
| O1—S1—N1—C8 | −65.38 (11) | C9—C10—C15—C14 | 178.24 (14) |
| C1—S1—N1—C8 | 47.13 (11) | C6—C7—C16—C17 | −4.9 (3) |
| O2—S1—N1—C9 | 28.63 (13) | C8—C7—C16—C17 | 169.70 (15) |
| O1—S1—N1—C9 | 158.17 (11) | C7—C16—C17—O4 | −7.5 (3) |
| C1—S1—N1—C9 | −89.32 (12) | C7—C16—C17—O3 | 174.59 (16) |
| O6—S2—N2—C25 | −164.94 (10) | O6—S2—C18—C19 | −49.22 (15) |
| O5—S2—N2—C25 | 65.20 (11) | O5—S2—C18—C19 | 81.24 (13) |
| C18—S2—N2—C25 | −48.23 (11) | N2—S2—C18—C19 | −165.08 (12) |
| O6—S2—N2—C26 | −28.22 (13) | O6—S2—C18—C23 | 132.05 (13) |
| O5—S2—N2—C26 | −158.09 (11) | O5—S2—C18—C23 | −97.48 (13) |
| C18—S2—N2—C26 | 88.48 (12) | N2—S2—C18—C23 | 16.19 (14) |
| O2—S1—C1—C2 | 48.83 (14) | C23—C18—C19—C20 | 0.8 (2) |
| O1—S1—C1—C2 | −80.91 (13) | S2—C18—C19—C20 | −177.93 (13) |
| N1—S1—C1—C2 | 165.80 (12) | C18—C19—C20—C21 | 0.6 (3) |
| O2—S1—C1—C6 | −136.40 (12) | C19—C20—C21—C22 | −0.6 (2) |
| O1—S1—C1—C6 | 93.86 (13) | C20—C21—C22—C23 | −1.0 (2) |
| N1—S1—C1—C6 | −19.43 (14) | C21—C22—C23—C18 | 2.3 (2) |
| C6—C1—C2—C3 | −4.0 (2) | C21—C22—C23—C24 | 180.00 (14) |
| S1—C1—C2—C3 | 170.69 (12) | C19—C18—C23—C22 | −2.2 (2) |
| C1—C2—C3—C4 | −2.9 (2) | S2—C18—C23—C22 | 176.43 (11) |
| C2—C3—C4—C5 | 5.6 (2) | C19—C18—C23—C24 | −179.98 (14) |
| C3—C4—C5—C6 | −1.4 (2) | S2—C18—C23—C24 | −1.3 (2) |
| C4—C5—C6—C1 | −5.3 (2) | C22—C23—C24—C33 | 18.1 (2) |
| C4—C5—C6—C7 | 175.82 (14) | C18—C23—C24—C33 | −164.34 (16) |
| C2—C1—C6—C5 | 8.0 (2) | C22—C23—C24—C25 | −160.80 (13) |
| S1—C1—C6—C5 | −166.50 (11) | C18—C23—C24—C25 | 16.81 (19) |
| C2—C1—C6—C7 | −173.07 (14) | C26—N2—C25—C24 | −67.74 (16) |
| S1—C1—C6—C7 | 12.41 (19) | S2—N2—C25—C24 | 70.24 (14) |
| C5—C6—C7—C16 | −37.3 (2) | C33—C24—C25—N2 | 128.86 (14) |
| C1—C6—C7—C16 | 143.83 (16) | C23—C24—C25—N2 | −52.10 (17) |
| C5—C6—C7—C8 | 147.93 (14) | C25—N2—C26—C27 | −77.84 (15) |
| C1—C6—C7—C8 | −30.93 (19) | S2—N2—C26—C27 | 147.39 (11) |
| C9—N1—C8—C7 | 67.11 (16) | N2—C26—C27—C28 | 117.32 (16) |
| S1—N1—C8—C7 | −70.46 (14) | N2—C26—C27—C32 | −61.75 (19) |
| C16—C7—C8—N1 | −115.16 (15) | C32—C27—C28—F4 | 179.40 (14) |
| C6—C7—C8—N1 | 60.14 (16) | C26—C27—C28—F4 | 0.3 (2) |
| C8—N1—C9—C10 | 76.81 (16) | C32—C27—C28—C29 | −0.7 (2) |
| S1—N1—C9—C10 | −148.39 (11) | C26—C27—C28—C29 | −179.81 (16) |
| N1—C9—C10—C11 | −124.09 (16) | F4—C28—C29—C30 | −179.77 (15) |
| N1—C9—C10—C15 | 58.04 (19) | C27—C28—C29—C30 | 0.3 (3) |
| C15—C10—C11—F1 | 178.93 (14) | C28—C29—C30—F5 | 178.65 (15) |
| C9—C10—C11—F1 | 1.0 (2) | C28—C29—C30—C31 | 0.1 (3) |
| C15—C10—C11—C12 | −0.6 (2) | F5—C30—C31—F6 | 0.6 (2) |
| C9—C10—C11—C12 | −178.53 (15) | C29—C30—C31—F6 | 179.15 (15) |
| F1—C11—C12—C13 | −179.90 (15) | F5—C30—C31—C32 | −178.77 (14) |
| C10—C11—C12—C13 | −0.4 (3) | C29—C30—C31—C32 | −0.2 (3) |

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|---|---|---|---|
| C11—C12—C13—F2 | −178.60 (14) | F6—C31—C32—C27 | −179.54 (13) |
| C11—C12—C13—C14 | 1.7 (2) | C30—C31—C32—C27 | −0.2 (2) |
| F2—C13—C14—F3 | −2.4 (2) | C28—C27—C32—C31 | 0.6 (2) |
| C12—C13—C14—F3 | 177.31 (15) | C26—C27—C32—C31 | 179.73 (14) |
| F2—C13—C14—C15 | 178.23 (14) | C23—C24—C33—C34 | 1.9 (3) |
| C12—C13—C14—C15 | −2.1 (2) | C25—C24—C33—C34 | −179.25 (15) |
| F3—C14—C15—C10 | −178.34 (14) | C24—C33—C34—O8 | 14.6 (3) |
| C13—C14—C15—C10 | 1.0 (2) | C24—C33—C34—O7 | −168.18 (17) |

*Hydrogen-bond geometry (Å, º)*

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| O3—H3$O$···O8[i] | 0.85 (3) | 1.86 (3) | 2.7063 (17) | 172 (3) |
| O7—H7$O$···O4[ii] | 0.92 (3) | 1.73 (3) | 2.6473 (17) | 177 (2) |
| C15—H15···O6 | 0.95 | 2.34 | 3.267 (2) | 165 |
| C32—H32···O2 | 0.95 | 2.61 | 3.539 (2) | 165 |

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