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# Crystal structure of (2*Z*)-2-{(5*Z*)-5-[3-fluoro-2-(4-phenylpiperidin-1-yl)benzylidene]-4-oxo-3-(*p*-tolyl)-1,3-thiazolidin-2-ylidene}-*N*-(*p*-tolyl)ethanethioamide dimethyl sulfoxide monosolvate

**Liliya Khamidullina,[a]* Konstantin Obydennov,[a] Pavel Slepukhin[b] and Yury Morzherin[a]**

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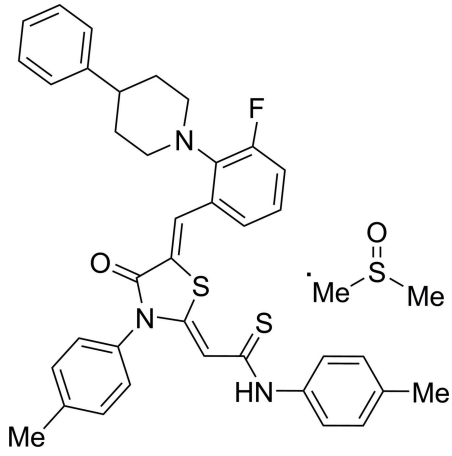
The title compound, $C_{37}H_{34}FN_3OS_2\cdot C_2H_6OS$, was obtained by the Knoevenagel condensation. The thiazolidine ring is essentially planar (r.m.s. deviation = 0.025 Å) and forms dihedral angles of 4.2 (3), 68.60 (14) and 39.57 (15)° with the attached thioamide group, *p*-tolyl group benzene ring and fluoro-substituted benzene ring, respectively. The exocyclic double bonds are in a *Z* configuration. In the crystal, the dimethyl sulfoxide solvent molecule is connected to the main molecule *via* an N—H···O hydrogen bond. Weak C—H···O hydrogen bonds link the components of the structure into a two-dimensional network parallel to $(10\bar{1})$. Weak intramolecular C—H···S hydrogen bonds are also observed. The crystal is an inversion twin with a ratio of twin components 0.78 (2):0.22 (6).

**Keywords:** crystal structure; thioamide; exocyclic double bond; thiazolidine; hydrogen bonding.

**CCDC reference**: 1423184

## 1. Related literature

For non-covalent interactions, see: Minkin & Minyaev (2001); Bjernemose *et al.* (2003). For the biological activity of thiazolidines, see: Nazreen *et al.* (2015); Tripathi *et al.* (2014). For docking investigations of thiazolidines, see: Sharma *et al.* (2015); Miyata *et al.* (2013). For materials applications of thiazolidines, see: Matsui *et al.* (2010). For the synthesis of related compounds, see: Obydennov *et al.* (2014).




## 2. Experimental

### 2.1. Crystal data

$C_{37}H_{34}FN_3OS_2\cdot C_2H_6OS$
$M_r$ = 697.92
Monoclinic, $P2_1$
$a$ = 9.8539 (5) Å
$b$ = 9.8671 (5) Å
$c$ = 18.1633 (8) Å
$\beta$ = 100.578 (5)°
$V$ = 1736.01 (14) Å$^3$
$Z$ = 2
Mo $K\alpha$ radiation
$\mu$ = 0.26 mm$^{-1}$
$T$ = 150 K
0.2 × 0.14 × 0.08 mm

### 2.2. Data collection

Agilent Xcalibur Eos diffractometer
Absorption correction: multi-scan (*CrysAlis PRO*; Agilent, 2013)
$T_{min}$ = 0.942, $T_{max}$ = 1.000
9751 measured reflections
7519 independent reflections
5344 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.029

### 2.3. Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.046
$wR(F^2)$ = 0.089
$S$ = 1.00
4992 reflections
437 parameters
1 restraint
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.63 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.48 e Å$^{-3}$
Absolute structure: Flack (1983), 2527 Friedel pairs
Absolute structure parameter: 0.22 (6)

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| N1—H1···O3 | 0.86 | 1.97 | 2.806 (4) | 164 |
| C8—H8···S1 | 0.93 | 2.68 | 3.224 (3) | 118 |
| C19—H19*B*···O2$^{i}$ | 0.97 | 2.53 | 3.398 (4) | 149 |
| C32—H32*A*···O3$^{ii}$ | 0.96 | 2.54 | 3.423 (5) | 152 |
| C37—H37···S2 | 0.93 | 2.58 | 3.210 (4) | 125 |

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

Data collection: *CrysAlis PRO* (Agilent, 2013); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis PRO*; program(s) used to solve structure: *SUPERFLIP* (Palatinus & Chapuis, 2007) and *PLATON* (Spek, 2009); program(s) used to refine structure: *SHELXS97* (Sheldrick, 2008); molecular graphics: *OLEX2* (Dolomanov *et al.*, 2009) and *publCIF* (Westrip, 2010); software used to prepare material for publication: *OLEX2* and *publCIF*.

## Acknowledgements

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Supporting information for this paper is available from the IUCr electronic archives (Reference: LH5784).

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# supporting information

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# Crystal structure of (2*Z*)-2-{(5*Z*)-5-[3-fluoro-2-(4-phenylpiperidin-1-yl)benzylidene]-4-oxo-3-(*p*-tolyl)-1,3-thiazolidin-2-ylidene}-*N*-(*p*-tolyl)ethanethioamide dimethyl sulfoxide monosolvate

**Liliya Khamidullina, Konstantin Obydennov, Pavel Slepukhin and Yury Morzherin**

## S1. Chemical context

Thiazolidines are an important class of heteroaromatic compounds and have widespread applications from ranging from pharmaceuticals (Tripathi *et al.*, 2014; Nazreen *et al.*, 2015) to materials (Matsui *et al.*, 2010). The structure determined using X-ray crystallography is useful to perform a docking screen, which is frequently used to predict the binding orientation of potential ligands to their targets in order to in turn predict the affinity and activity of the ligands (Miyata *et al.*, 2013; Sharma *et al.*, 2015). Consequently, we have synthesized the title compound and its crystal structure is presented herein.

## S2. Structural commentary

The molecular structure of the title compound is shown in Fig. 1. The thioamide group is approximately in the plane of the thiazolidine ring forming a short S1···S2 contact (Minkin & Minyaev, 2001) with a distance of 2.972 (1) Å. This contact is observed for similar compounds containing a five-membered quasi-ring involving S···S interactions (Bjernemose *et al.*, 2003; Obydennov *et al.*, 2014). The *p*-tolyl group benzene ring and thiazolidine ring form a dihedral angle of 68.60 (14)°. The piperidine ring is in a chair conformation and both the aryl substituents are in equatorial positions. The sum of the bond angles around the thiazolidine ring N3 atom (360.0°) indicates $sp^2$ hybridization. The exocyclic double bonds are in a *Z*-configuration. In the crystal, the dimethylsulfoxide solvent molecule is connected to the main molecule via an N—H···O hydrogen bond. Weak C—H···O hydrogen bonds link the components of the structure into a two-dimensional network parallel to $(10\bar{1})$. Weak intramolecular C—H···S hydrogen bonds are also observed.

## S3. Synthesis and crystallization

\ (2*Z*)-2-[(5*Z*)-5-(3-fluoro-2-(4-phenylpiperidin-1-yl)benzylidene)-\ 4-oxo-3-(*p*-tolyl)-1,3-thiazolidin-2-ylidene]-*N*-(*p*-\ tolyl)ethanethioamide was prepared from (2*Z*)-*N*-(4-methylphenyl)-2-[3-(4-methylphenyl)-4-oxo-1,3-\ thiazolidin-2-ylidene]ethanethioamide by the Knoevenagel condensation. To a suspension of (2*Z*)-*N*-(4-methylphenyl)-2-[3-(4-methylphenyl)-4-oxo-1,3-\ thiazolidin-2-ylidene]ethanethioamide (248 mg, 0.7 mmol) in *n*-butanol (10 ml) were added 3-fluoro-2-(4-phenylpiperidin-1-yl)benzaldehyde (397 mg, 1.4 mmol) and piperidine (0.06 ml, 0.7 mmol) at room temperature. The mixture was stirred at refluxe for 12 h. After cooling to 255K the crude product was filtered off, recrystallized from ethanol, washed by cooled ethanol and dried *in vacuo*. Yield: 126 mg (29%). $^1$H NMR (400 MHz, DMSO-$d_6$, $\delta$, p.p.m.): 1.68–1.92 (4H, *br.m.*, $CH_2$), 2.26 (1H, *s.*, Me), 2.43 (1H, *s.*, Me), 2.70 (1H, *br.m.*, CH), 3.02–3.20 (2H, *br.m.*, $CH_2$), 3.20–3.32 (2H, *br.m.*, $CH_2$), 6.19 (1H, *s.*, CH=), 7.04–7.66 (15H, *m.*, ArH + CH=), 8.04 (1H, *s.*, ArH), 11.17 (1H, *s.*, NH). Needle-like orange single crystals suitable for X-ray diffraction studies were obtained by slow evaporation of a dimethyl sulfoxide solution of the title compound at room temperature. M.p. 431-433 K.

## S4. Refinement

Hydrogen atoms were placed in calculated positions with C—H = 0.93 - 0.98 Å, N—H = 0.86 Å and included in a riding-model approximation $U_{iso}(H) = 1.2U_{eq}(C,N)$ or $1.5U_{eq}(C)$ for methyl H atoms.

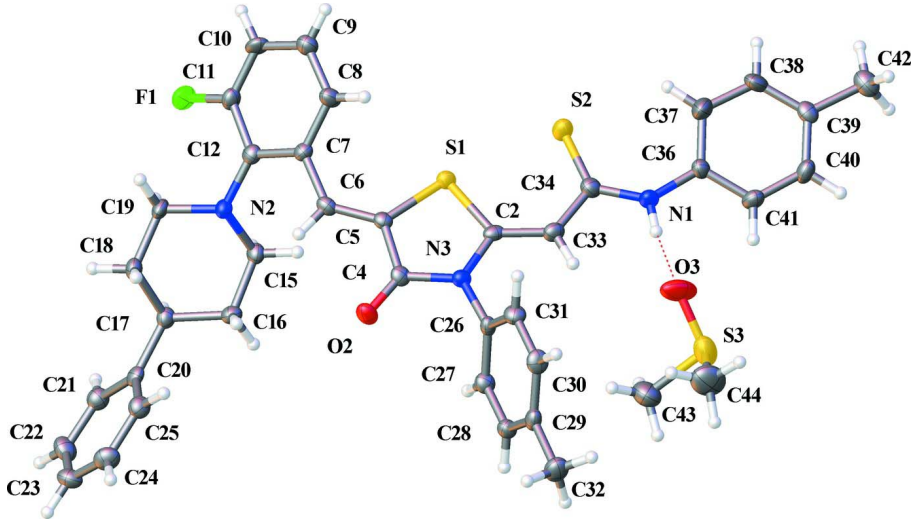


**Figure 1**

The molecular structure of the title compound showing 50% probability displacement ellipsoids.

**(2*Z*)-2-{(5*Z*)-5-[3-Fluoro-2-(4-phenylpiperidin-1-yl)benzylidene]-4-oxo-3-(*p*-tolyl)-1,3-thiazolidin-2-ylidene}-*N*-(*p*-tolyl)ethanethioamide dimethyl sulfoxide monosolvate**

*Crystal data*

$C_{37}H_{34}FN_3OS_2 \cdot C_2H_6OS$
$M_r = 697.92$
Monoclinic, $P2_1$
$a = 9.8539$ (5) Å
$b = 9.8671$ (5) Å
$c = 18.1633$ (8) Å
$\beta = 100.578$ (5)°
$V = 1736.01$ (14) Å$^3$
$Z = 2$
$F(000) = 736$
$D_x = 1.335$ Mg m$^{-3}$
Melting point = 160–158 K
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 2519 reflections
$\theta = 2.3$–$30.2°$
$\mu = 0.26$ mm$^{-1}$
$T = 150$ K
Block, orange
0.2 × 0.14 × 0.08 mm

*Data collection*

Agilent Xcalibur Eos diffractometer
Radiation source: Enhance (Mo) X-ray Source
Graphite monochromator
Detector resolution: 15.9555 pixels mm$^{-1}$
$\omega$ scans
Absorption correction: multi-scan (*CrysAlis PRO*; Agilent, 2013)
$T_{min} = 0.942$, $T_{max} = 1.000$
9751 measured reflections
7519 independent reflections
5344 reflections with $I > 2\sigma(I)$
$R_{int} = 0.029$
$\theta_{max} = 30.8°$, $\theta_{min} = 2.1°$
$h = -13 \rightarrow 12$
$k = -14 \rightarrow 14$
$l = -25 \rightarrow 25$

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.046$
$wR(F^2) = 0.089$
$S = 1.00$
4992 reflections
437 parameters
1 restraint
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.021P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.63$ e Å$^{-3}$
$\Delta\rho_{min} = -0.48$ e Å$^{-3}$
Absolute structure: Flack (1983), 2527 Friedel pairs
Absolute structure parameter: 0.22 (6)

*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 | 0.53305 (8) | 0.25119 (8) | 0.25856 (4) | 0.02326 (18) |
| S3 | 0.80859 (11) | 0.72542 (12) | 0.55377 (5) | 0.0473 (3) |
| O2 | 0.5650 (2) | 0.5633 (2) | 0.13469 (12) | 0.0293 (5) |
| F1 | 0.15403 (19) | −0.03590 (19) | −0.04379 (10) | 0.0352 (5) |
| C7 | 0.4153 (3) | 0.1509 (3) | 0.08448 (17) | 0.0211 (7) |
| N2 | 0.2325 (2) | 0.2421 (3) | −0.01238 (13) | 0.0214 (5) |
| N1 | 0.6889 (3) | 0.3429 (3) | 0.50937 (15) | 0.0294 (7) |
| H1 | 0.7187 | 0.4250 | 0.5119 | 0.035* |
| C20 | 0.0297 (3) | 0.5866 (3) | −0.13326 (17) | 0.0220 (7) |
| C2 | 0.6082 (3) | 0.3936 (3) | 0.30804 (18) | 0.0201 (7) |
| C34 | 0.6393 (3) | 0.3019 (3) | 0.43872 (18) | 0.0268 (8) |
| C39 | 0.7442 (3) | 0.1644 (4) | 0.72440 (18) | 0.0252 (8) |
| C29 | 0.8222 (3) | 0.8738 (3) | 0.31806 (17) | 0.0245 (8) |
| C11 | 0.2678 (3) | −0.0075 (3) | 0.00875 (17) | 0.0245 (7) |
| C21 | −0.1030 (3) | 0.6112 (3) | −0.17432 (18) | 0.0278 (8) |
| H21 | −0.1743 | 0.5523 | −0.1692 | 0.033* |
| C12 | 0.3016 (3) | 0.1303 (3) | 0.02578 (17) | 0.0219 (7) |
| C19 | 0.1557 (3) | 0.2225 (3) | −0.08942 (16) | 0.0252 (7) |
| H19A | 0.0671 | 0.1808 | −0.0878 | 0.030* |
| H19B | 0.2070 | 0.1621 | −0.1164 | 0.030* |
| C26 | 0.6885 (3) | 0.6261 (3) | 0.28185 (16) | 0.0192 (7) |
| C10 | 0.3402 (3) | −0.1149 (3) | 0.04386 (18) | 0.0284 (8) |
| H10 | 0.3145 | −0.2032 | 0.0296 | 0.034* |

| | | | | |
|---|---|---|---|---|
| C31 | 0.8311 (3) | 0.6293 (3) | 0.30665 (17) | 0.0255 (8) |
| H31 | 0.8822 | 0.5495 | 0.3109 | 0.031* |
| C33 | 0.6496 (3) | 0.4047 (3) | 0.38338 (18) | 0.0243 (7) |
| H33 | 0.6886 | 0.4870 | 0.4012 | 0.029* |
| C24 | 0.1034 (4) | 0.7911 (3) | −0.1875 (2) | 0.0329 (9) |
| H24 | 0.1724 | 0.8537 | −0.1911 | 0.040* |
| O3 | 0.8366 (3) | 0.5875 (3) | 0.52409 (16) | 0.0588 (8) |
| C38 | 0.7181 (4) | 0.0861 (4) | 0.6629 (2) | 0.0407 (10) |
| H38 | 0.7130 | −0.0073 | 0.6689 | 0.049* |
| C17 | 0.0588 (3) | 0.4582 (3) | −0.08805 (17) | 0.0234 (7) |
| H17 | −0.0305 | 0.4185 | −0.0835 | 0.028* |
| C30 | 0.8959 (3) | 0.7534 (4) | 0.32496 (16) | 0.0267 (7) |
| H30 | 0.9908 | 0.7555 | 0.3422 | 0.032* |
| C28 | 0.6801 (3) | 0.8663 (3) | 0.29401 (17) | 0.0245 (7) |
| H28 | 0.6283 | 0.9457 | 0.2897 | 0.029* |
| C18 | 0.1332 (3) | 0.3556 (3) | −0.12984 (17) | 0.0260 (7) |
| H18A | 0.0791 | 0.3408 | −0.1794 | 0.031* |
| H18B | 0.2218 | 0.3926 | −0.1357 | 0.031* |
| C15 | 0.1606 (3) | 0.3354 (3) | 0.02973 (17) | 0.0237 (7) |
| H15A | 0.2128 | 0.3455 | 0.0802 | 0.028* |
| H15B | 0.0706 | 0.2987 | 0.0331 | 0.028* |
| C6 | 0.4630 (3) | 0.2886 (3) | 0.10419 (17) | 0.0209 (7) |
| H6 | 0.4554 | 0.3498 | 0.0647 | 0.025* |
| N3 | 0.6215 (3) | 0.5000 (2) | 0.25863 (14) | 0.0207 (6) |
| C36 | 0.7022 (3) | 0.2793 (3) | 0.58018 (18) | 0.0248 (8) |
| C23 | −0.0257 (4) | 0.8094 (3) | −0.22808 (19) | 0.0303 (8) |
| H23 | −0.0436 | 0.8830 | −0.2604 | 0.036* |
| C22 | −0.1303 (3) | 0.7198 (4) | −0.22178 (18) | 0.0334 (8) |
| H22 | −0.2185 | 0.7329 | −0.2495 | 0.040* |
| C9 | 0.4511 (3) | −0.0914 (3) | 0.10031 (18) | 0.0282 (8) |
| H9 | 0.5014 | −0.1635 | 0.1245 | 0.034* |
| C25 | 0.1329 (3) | 0.6792 (3) | −0.14067 (17) | 0.0285 (8) |
| H25 | 0.2220 | 0.6662 | −0.1142 | 0.034* |
| C16 | 0.1431 (3) | 0.4732 (3) | −0.00841 (17) | 0.0249 (7) |
| H16A | 0.2330 | 0.5112 | −0.0107 | 0.030* |
| H16B | 0.0961 | 0.5344 | 0.0203 | 0.030* |
| C27 | 0.6140 (3) | 0.7448 (4) | 0.27641 (16) | 0.0236 (7) |
| H27 | 0.5187 | 0.7427 | 0.2608 | 0.028* |
| C4 | 0.5671 (3) | 0.4781 (3) | 0.18329 (17) | 0.0212 (7) |
| C41 | 0.7255 (3) | 0.3600 (3) | 0.64298 (18) | 0.0289 (8) |
| H41 | 0.7270 | 0.4537 | 0.6378 | 0.035* |
| C42 | 0.7674 (3) | 0.1067 (4) | 0.80330 (18) | 0.0376 (9) |
| H42A | 0.7368 | 0.0142 | 0.8016 | 0.056* |
| H42B | 0.7162 | 0.1588 | 0.8335 | 0.056* |
| H42C | 0.8639 | 0.1106 | 0.8247 | 0.056* |
| C5 | 0.5160 (3) | 0.3375 (3) | 0.17185 (17) | 0.0191 (7) |
| C37 | 0.6984 (4) | 0.1388 (4) | 0.5902 (2) | 0.0493 (11) |
| H37 | 0.6829 | 0.0811 | 0.5490 | 0.059* |

| | | | | |
|---|---|---|---|---|
| C8 | 0.4869 (3) | 0.0401 (3) | 0.12070 (18) | 0.0273 (8) |
| H8 | 0.5607 | 0.0556 | 0.1597 | 0.033* |
| C40 | 0.7468 (4) | 0.3030 (4) | 0.71362 (19) | 0.0304 (8) |
| H40 | 0.7634 | 0.3596 | 0.7552 | 0.036* |
| C43 | 0.6849 (4) | 0.7983 (4) | 0.4815 (2) | 0.0515 (11) |
| H43A | 0.7139 | 0.7859 | 0.4343 | 0.077* |
| H43B | 0.6768 | 0.8934 | 0.4910 | 0.077* |
| H43C | 0.5972 | 0.7552 | 0.4802 | 0.077* |
| C32 | 0.8930 (4) | 1.0061 (3) | 0.33599 (19) | 0.0376 (9) |
| H32A | 0.9678 | 0.9949 | 0.3776 | 0.056* |
| H32B | 0.8285 | 1.0710 | 0.3487 | 0.056* |
| H32C | 0.9284 | 1.0377 | 0.2932 | 0.056* |
| S2 | 0.56650 (10) | 0.15033 (9) | 0.41505 (5) | 0.0337 (2) |
| C44 | 0.9535 (4) | 0.8225 (4) | 0.5416 (3) | 0.0622 (13) |
| H44A | 1.0315 | 0.7976 | 0.5790 | 0.093* |
| H44B | 0.9337 | 0.9170 | 0.5464 | 0.093* |
| H44C | 0.9738 | 0.8056 | 0.4927 | 0.093* |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| S1 | 0.0272 (4) | 0.0181 (4) | 0.0226 (4) | −0.0025 (4) | −0.0007 (3) | 0.0005 (4) |
| S3 | 0.0589 (7) | 0.0459 (7) | 0.0323 (5) | −0.0111 (6) | −0.0045 (4) | 0.0061 (5) |
| O2 | 0.0355 (14) | 0.0227 (13) | 0.0269 (13) | −0.0079 (11) | −0.0017 (10) | 0.0060 (11) |
| F1 | 0.0356 (12) | 0.0279 (11) | 0.0369 (12) | −0.0098 (9) | −0.0068 (9) | −0.0063 (10) |
| C7 | 0.0237 (16) | 0.0191 (16) | 0.0204 (16) | 0.0005 (15) | 0.0037 (13) | −0.0021 (15) |
| N2 | 0.0234 (13) | 0.0218 (14) | 0.0178 (13) | 0.0016 (13) | 0.0006 (10) | −0.0025 (13) |
| N1 | 0.0438 (18) | 0.0172 (15) | 0.0239 (15) | −0.0033 (13) | −0.0025 (13) | −0.0005 (13) |
| C20 | 0.0260 (17) | 0.0236 (18) | 0.0174 (16) | 0.0007 (15) | 0.0063 (13) | −0.0060 (15) |
| C2 | 0.0161 (15) | 0.0152 (16) | 0.0278 (18) | 0.0022 (13) | 0.0010 (13) | −0.0025 (15) |
| C34 | 0.0283 (18) | 0.0236 (17) | 0.0261 (19) | 0.0015 (15) | −0.0019 (14) | 0.0015 (16) |
| C39 | 0.0192 (16) | 0.030 (2) | 0.0256 (18) | 0.0035 (16) | 0.0018 (13) | 0.0053 (17) |
| C29 | 0.0332 (19) | 0.0246 (19) | 0.0156 (16) | −0.0063 (15) | 0.0038 (14) | −0.0011 (16) |
| C11 | 0.0261 (18) | 0.0248 (19) | 0.0214 (17) | −0.0067 (15) | 0.0009 (14) | −0.0031 (16) |
| C21 | 0.0260 (18) | 0.028 (2) | 0.0291 (19) | −0.0013 (15) | 0.0045 (14) | −0.0018 (16) |
| C12 | 0.0230 (16) | 0.0230 (18) | 0.0202 (16) | 0.0000 (14) | 0.0056 (13) | −0.0017 (15) |
| C19 | 0.0303 (17) | 0.0243 (19) | 0.0187 (16) | 0.0038 (15) | −0.0013 (13) | −0.0080 (16) |
| C26 | 0.0219 (16) | 0.0203 (18) | 0.0142 (15) | −0.0052 (14) | 0.0000 (12) | 0.0002 (14) |
| C10 | 0.039 (2) | 0.0132 (16) | 0.033 (2) | −0.0067 (15) | 0.0070 (16) | −0.0013 (16) |
| C31 | 0.0233 (17) | 0.0248 (19) | 0.0282 (18) | 0.0055 (15) | 0.0043 (14) | 0.0000 (16) |
| C33 | 0.0238 (18) | 0.0196 (17) | 0.0277 (18) | −0.0025 (14) | 0.0001 (14) | −0.0026 (15) |
| C24 | 0.034 (2) | 0.027 (2) | 0.039 (2) | −0.0075 (16) | 0.0115 (17) | 0.0002 (18) |
| O3 | 0.0551 (18) | 0.0225 (15) | 0.086 (2) | −0.0061 (13) | −0.0216 (15) | −0.0003 (15) |
| C38 | 0.058 (3) | 0.0203 (19) | 0.036 (2) | 0.0052 (18) | −0.0114 (18) | 0.0069 (18) |
| C17 | 0.0219 (17) | 0.0264 (18) | 0.0206 (17) | 0.0001 (15) | 0.0007 (13) | −0.0021 (16) |
| C30 | 0.0173 (15) | 0.033 (2) | 0.0284 (17) | −0.0060 (16) | 0.0008 (12) | −0.0008 (18) |
| C28 | 0.0293 (19) | 0.0207 (18) | 0.0222 (17) | −0.0009 (15) | 0.0011 (14) | 0.0017 (15) |
| C18 | 0.0311 (18) | 0.0282 (19) | 0.0170 (16) | 0.0015 (15) | −0.0004 (14) | −0.0032 (15) |

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|---|---|---|---|---|---|---|
| C15 | 0.0258 (18) | 0.0267 (19) | 0.0183 (16) | 0.0031 (15) | 0.0035 (13) | −0.0015 (15) |
| C6 | 0.0193 (16) | 0.0212 (18) | 0.0224 (17) | 0.0007 (13) | 0.0038 (13) | 0.0057 (15) |
| N3 | 0.0210 (13) | 0.0174 (14) | 0.0221 (14) | −0.0006 (11) | −0.0004 (11) | 0.0001 (12) |
| C36 | 0.0294 (18) | 0.0213 (19) | 0.0208 (17) | −0.0012 (14) | −0.0025 (13) | 0.0010 (15) |
| C23 | 0.033 (2) | 0.0235 (18) | 0.035 (2) | 0.0049 (16) | 0.0070 (16) | 0.0063 (16) |
| C22 | 0.0300 (18) | 0.039 (2) | 0.0292 (18) | 0.0072 (17) | 0.0002 (14) | 0.0059 (19) |
| C9 | 0.033 (2) | 0.0239 (19) | 0.0266 (19) | −0.0006 (16) | 0.0029 (15) | 0.0031 (16) |
| C25 | 0.0259 (18) | 0.030 (2) | 0.0282 (18) | 0.0019 (15) | 0.0018 (14) | −0.0015 (17) |
| C16 | 0.0289 (18) | 0.0191 (17) | 0.0261 (18) | 0.0022 (15) | 0.0034 (14) | −0.0020 (15) |
| C27 | 0.0194 (15) | 0.0254 (17) | 0.0245 (16) | −0.0014 (16) | 0.0002 (12) | 0.0009 (17) |
| C4 | 0.0154 (15) | 0.0242 (18) | 0.0226 (17) | −0.0004 (14) | 0.0000 (13) | 0.0011 (16) |
| C41 | 0.039 (2) | 0.0189 (18) | 0.0287 (19) | −0.0034 (16) | 0.0064 (16) | −0.0031 (16) |
| C42 | 0.035 (2) | 0.042 (2) | 0.036 (2) | 0.0032 (17) | 0.0043 (17) | 0.009 (2) |
| C5 | 0.0170 (15) | 0.0185 (17) | 0.0212 (17) | 0.0024 (13) | 0.0022 (12) | 0.0019 (14) |
| C37 | 0.082 (3) | 0.030 (2) | 0.029 (2) | 0.011 (2) | −0.009 (2) | −0.008 (2) |
| C8 | 0.0299 (19) | 0.0206 (18) | 0.0283 (19) | −0.0017 (15) | −0.0030 (15) | 0.0034 (16) |
| C40 | 0.040 (2) | 0.0290 (19) | 0.0216 (18) | −0.0070 (17) | 0.0050 (15) | −0.0071 (17) |
| C43 | 0.064 (3) | 0.041 (3) | 0.047 (3) | 0.011 (2) | 0.001 (2) | 0.008 (2) |
| C32 | 0.048 (2) | 0.029 (2) | 0.035 (2) | −0.0099 (17) | 0.0035 (18) | −0.0025 (18) |
| S2 | 0.0512 (6) | 0.0236 (5) | 0.0245 (5) | −0.0075 (5) | 0.0020 (4) | −0.0012 (4) |
| C44 | 0.060 (3) | 0.044 (3) | 0.075 (3) | −0.020 (2) | −0.006 (2) | 0.002 (3) |

*Geometric parameters (Å, º)*

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| S1—C2 | 1.757 (3) | C24—H24 | 0.9300 |
| S1—C5 | 1.771 (3) | C38—C37 | 1.399 (5) |
| S3—O3 | 1.508 (3) | C38—H38 | 0.9300 |
| S3—C44 | 1.766 (4) | C17—C18 | 1.531 (4) |
| S3—C43 | 1.771 (4) | C17—C16 | 1.537 (4) |
| O2—C4 | 1.217 (3) | C17—H17 | 0.9800 |
| F1—C11 | 1.361 (3) | C30—H30 | 0.9300 |
| C7—C8 | 1.398 (4) | C28—C27 | 1.374 (4) |
| C7—C12 | 1.413 (4) | C28—H28 | 0.9300 |
| C7—C6 | 1.460 (4) | C18—H18A | 0.9700 |
| N2—C12 | 1.410 (4) | C18—H18B | 0.9700 |
| N2—C15 | 1.461 (4) | C15—C16 | 1.521 (4) |
| N2—C19 | 1.476 (3) | C15—H15A | 0.9700 |
| N1—C34 | 1.349 (4) | C15—H15B | 0.9700 |
| N1—C36 | 1.416 (4) | C6—C5 | 1.334 (4) |
| N1—H1 | 0.8600 | C6—H6 | 0.9300 |
| C20—C25 | 1.392 (4) | N3—C4 | 1.392 (4) |
| C20—C21 | 1.402 (4) | C36—C41 | 1.376 (4) |
| C20—C17 | 1.509 (4) | C36—C37 | 1.400 (5) |
| C2—C33 | 1.358 (4) | C23—C22 | 1.378 (4) |
| C2—N3 | 1.402 (4) | C23—H23 | 0.9300 |
| C34—C33 | 1.444 (4) | C22—H22 | 0.9300 |
| C34—S2 | 1.680 (3) | C9—C8 | 1.377 (4) |
| C39—C38 | 1.344 (5) | C9—H9 | 0.9300 |

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| C39—C40 | 1.382 (4) | C25—H25 | 0.9300 |
| C39—C42 | 1.520 (4) | C16—H16A | 0.9700 |
| C29—C30 | 1.387 (4) | C16—H16B | 0.9700 |
| C29—C28 | 1.390 (4) | C27—H27 | 0.9300 |
| C29—C32 | 1.487 (4) | C4—C5 | 1.477 (4) |
| C11—C10 | 1.368 (4) | C41—C40 | 1.381 (4) |
| C11—C12 | 1.420 (4) | C41—H41 | 0.9300 |
| C21—C22 | 1.370 (4) | C42—H42A | 0.9600 |
| C21—H21 | 0.9300 | C42—H42B | 0.9600 |
| C19—C18 | 1.501 (4) | C42—H42C | 0.9600 |
| C19—H19A | 0.9700 | C37—H37 | 0.9300 |
| C19—H19B | 0.9700 | C8—H8 | 0.9300 |
| C26—C27 | 1.376 (4) | C40—H40 | 0.9300 |
| C26—C31 | 1.395 (4) | C43—H43A | 0.9600 |
| C26—N3 | 1.436 (4) | C43—H43B | 0.9600 |
| C10—C9 | 1.374 (4) | C43—H43C | 0.9600 |
| C10—H10 | 0.9300 | C32—H32A | 0.9600 |
| C31—C30 | 1.393 (5) | C32—H32B | 0.9600 |
| C31—H31 | 0.9300 | C32—H32C | 0.9600 |
| C33—H33 | 0.9300 | C44—H44A | 0.9600 |
| C24—C23 | 1.361 (5) | C44—H44B | 0.9600 |
| C24—C25 | 1.391 (4) | C44—H44C | 0.9600 |

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| C2—S1—C5 | 91.86 (15) | C19—C18—C17 | 112.1 (2) |
| O3—S3—C44 | 103.86 (19) | C19—C18—H18A | 109.2 |
| O3—S3—C43 | 104.35 (17) | C17—C18—H18A | 109.2 |
| C44—S3—C43 | 98.6 (2) | C19—C18—H18B | 109.2 |
| C8—C7—C12 | 120.3 (3) | C17—C18—H18B | 109.2 |
| C8—C7—C6 | 120.0 (3) | H18A—C18—H18B | 107.9 |
| C12—C7—C6 | 119.6 (3) | N2—C15—C16 | 110.5 (2) |
| C12—N2—C15 | 118.2 (2) | N2—C15—H15A | 109.6 |
| C12—N2—C19 | 118.7 (3) | C16—C15—H15A | 109.6 |
| C15—N2—C19 | 111.4 (2) | N2—C15—H15B | 109.6 |
| C34—N1—C36 | 133.5 (3) | C16—C15—H15B | 109.6 |
| C34—N1—H1 | 113.3 | H15A—C15—H15B | 108.1 |
| C36—N1—H1 | 113.3 | C5—C6—C7 | 128.0 (3) |
| C25—C20—C21 | 117.5 (3) | C5—C6—H6 | 116.0 |
| C25—C20—C17 | 122.3 (3) | C7—C6—H6 | 116.0 |
| C21—C20—C17 | 120.0 (3) | C4—N3—C2 | 116.7 (3) |
| C33—C2—N3 | 122.6 (3) | C4—N3—C26 | 119.8 (3) |
| C33—C2—S1 | 126.9 (2) | C2—N3—C26 | 123.5 (3) |
| N3—C2—S1 | 110.6 (2) | C41—C36—C37 | 118.0 (3) |
| N1—C34—C33 | 113.1 (3) | C41—C36—N1 | 118.0 (3) |
| N1—C34—S2 | 125.0 (2) | C37—C36—N1 | 123.9 (3) |
| C33—C34—S2 | 121.9 (3) | C24—C23—C22 | 120.6 (3) |
| C38—C39—C40 | 117.2 (3) | C24—C23—H23 | 119.7 |
| C38—C39—C42 | 122.7 (3) | C22—C23—H23 | 119.7 |
| C40—C39—C42 | 120.0 (3) | C21—C22—C23 | 119.3 (3) |

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| C30—C29—C28 | 117.6 (3) | C21—C22—H22 | 120.3 |
| C30—C29—C32 | 121.0 (3) | C23—C22—H22 | 120.3 |
| C28—C29—C32 | 121.4 (3) | C10—C9—C8 | 119.3 (3) |
| F1—C11—C10 | 117.3 (3) | C10—C9—H9 | 120.4 |
| F1—C11—C12 | 118.7 (3) | C8—C9—H9 | 120.4 |
| C10—C11—C12 | 124.0 (3) | C24—C25—C20 | 120.4 (3) |
| C22—C21—C20 | 121.8 (3) | C24—C25—H25 | 119.8 |
| C22—C21—H21 | 119.1 | C20—C25—H25 | 119.8 |
| C20—C21—H21 | 119.1 | C15—C16—C17 | 109.8 (3) |
| N2—C12—C7 | 120.2 (3) | C15—C16—H16A | 109.7 |
| N2—C12—C11 | 124.7 (3) | C17—C16—H16A | 109.7 |
| C7—C12—C11 | 115.1 (3) | C15—C16—H16B | 109.7 |
| N2—C19—C18 | 110.7 (3) | C17—C16—H16B | 109.7 |
| N2—C19—H19A | 109.5 | H16A—C16—H16B | 108.2 |
| C18—C19—H19A | 109.5 | C28—C27—C26 | 120.1 (3) |
| N2—C19—H19B | 109.5 | C28—C27—H27 | 119.9 |
| C18—C19—H19B | 109.5 | C26—C27—H27 | 119.9 |
| H19A—C19—H19B | 108.1 | O2—C4—N3 | 123.9 (3) |
| C27—C26—C31 | 119.8 (3) | O2—C4—C5 | 125.9 (3) |
| C27—C26—N3 | 120.4 (3) | N3—C4—C5 | 110.1 (3) |
| C31—C26—N3 | 119.7 (3) | C36—C41—C40 | 120.5 (3) |
| C11—C10—C9 | 119.5 (3) | C36—C41—H41 | 119.7 |
| C11—C10—H10 | 120.3 | C40—C41—H41 | 119.7 |
| C9—C10—H10 | 120.3 | C39—C42—H42A | 109.5 |
| C30—C31—C26 | 119.2 (3) | C39—C42—H42B | 109.5 |
| C30—C31—H31 | 120.4 | H42A—C42—H42B | 109.5 |
| C26—C31—H31 | 120.4 | C39—C42—H42C | 109.5 |
| C2—C33—C34 | 126.7 (3) | H42A—C42—H42C | 109.5 |
| C2—C33—H33 | 116.6 | H42B—C42—H42C | 109.5 |
| C34—C33—H33 | 116.6 | C6—C5—C4 | 122.3 (3) |
| C23—C24—C25 | 120.4 (3) | C6—C5—S1 | 127.0 (2) |
| C23—C24—H24 | 119.8 | C4—C5—S1 | 110.6 (2) |
| C25—C24—H24 | 119.8 | C38—C37—C36 | 119.3 (3) |
| C39—C38—C37 | 122.9 (3) | C38—C37—H37 | 120.4 |
| C39—C38—H38 | 118.6 | C36—C37—H37 | 120.4 |
| C37—C38—H38 | 118.6 | C9—C8—C7 | 121.9 (3) |
| C20—C17—C18 | 110.3 (2) | C9—C8—H8 | 119.1 |
| C20—C17—C16 | 116.6 (3) | C7—C8—H8 | 119.1 |
| C18—C17—C16 | 107.7 (2) | C41—C40—C39 | 122.1 (3) |
| C20—C17—H17 | 107.3 | C41—C40—H40 | 119.0 |
| C18—C17—H17 | 107.3 | C39—C40—H40 | 119.0 |
| C16—C17—H17 | 107.3 | C29—C32—H32A | 109.5 |
| C29—C30—C31 | 121.5 (3) | C29—C32—H32B | 109.5 |
| C29—C30—H30 | 119.3 | H32A—C32—H32B | 109.5 |
| C31—C30—H30 | 119.3 | C29—C32—H32C | 109.5 |
| C27—C28—C29 | 121.8 (3) | H32A—C32—H32C | 109.5 |
| C27—C28—H28 | 119.1 | H32B—C32—H32C | 109.5 |
| C29—C28—H28 | 119.1 | | |

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| C5—S1—C2—C33 | 178.6 (3) | C33—C2—N3—C4 | −176.1 (3) |
| C5—S1—C2—N3 | −1.4 (2) | S1—C2—N3—C4 | 3.9 (3) |
| C36—N1—C34—C33 | −179.1 (3) | C33—C2—N3—C26 | 4.7 (4) |
| C36—N1—C34—S2 | 3.2 (5) | S1—C2—N3—C26 | −175.3 (2) |
| C25—C20—C21—C22 | 1.8 (4) | C27—C26—N3—C4 | 66.9 (4) |
| C17—C20—C21—C22 | −173.5 (3) | C31—C26—N3—C4 | −110.0 (3) |
| C15—N2—C12—C7 | −64.4 (4) | C27—C26—N3—C2 | −113.9 (3) |
| C19—N2—C12—C7 | 155.6 (3) | C31—C26—N3—C2 | 69.2 (4) |
| C15—N2—C12—C11 | 117.2 (3) | C34—N1—C36—C41 | −164.0 (3) |
| C19—N2—C12—C11 | −22.8 (4) | C34—N1—C36—C37 | 18.6 (6) |
| C8—C7—C12—N2 | −177.8 (3) | C25—C24—C23—C22 | 2.0 (5) |
| C6—C7—C12—N2 | −1.4 (4) | C20—C21—C22—C23 | −1.6 (5) |
| C8—C7—C12—C11 | 0.7 (4) | C24—C23—C22—C21 | −0.3 (5) |
| C6—C7—C12—C11 | 177.1 (3) | C11—C10—C9—C8 | 0.3 (5) |
| F1—C11—C12—N2 | −5.7 (4) | C23—C24—C25—C20 | −1.8 (5) |
| C10—C11—C12—N2 | 176.6 (3) | C21—C20—C25—C24 | −0.1 (4) |
| F1—C11—C12—C7 | 175.8 (2) | C17—C20—C25—C24 | 175.1 (3) |
| C10—C11—C12—C7 | −1.9 (5) | N2—C15—C16—C17 | 59.9 (3) |
| C12—N2—C19—C18 | −159.8 (2) | C20—C17—C16—C15 | 178.9 (2) |
| C15—N2—C19—C18 | 57.7 (3) | C18—C17—C16—C15 | −56.6 (3) |
| F1—C11—C10—C9 | −176.3 (3) | C29—C28—C27—C26 | −0.5 (4) |
| C12—C11—C10—C9 | 1.4 (5) | C31—C26—C27—C28 | 1.2 (4) |
| C27—C26—C31—C30 | −0.5 (4) | N3—C26—C27—C28 | −175.7 (3) |
| N3—C26—C31—C30 | 176.4 (3) | C2—N3—C4—O2 | 176.2 (3) |
| N3—C2—C33—C34 | 179.5 (3) | C26—N3—C4—O2 | −4.6 (4) |
| S1—C2—C33—C34 | −0.6 (5) | C2—N3—C4—C5 | −4.8 (3) |
| N1—C34—C33—C2 | −179.8 (3) | C26—N3—C4—C5 | 174.5 (2) |
| S2—C34—C33—C2 | −2.0 (4) | C37—C36—C41—C40 | 1.1 (5) |
| C40—C39—C38—C37 | 2.0 (5) | N1—C36—C41—C40 | −176.5 (3) |
| C42—C39—C38—C37 | −179.2 (3) | C7—C6—C5—C4 | 176.7 (3) |
| C25—C20—C17—C18 | −73.6 (4) | C7—C6—C5—S1 | −4.7 (5) |
| C21—C20—C17—C18 | 101.5 (3) | O2—C4—C5—C6 | 1.3 (5) |
| C25—C20—C17—C16 | 49.6 (4) | N3—C4—C5—C6 | −177.7 (3) |
| C21—C20—C17—C16 | −135.3 (3) | O2—C4—C5—S1 | −177.6 (2) |
| C28—C29—C30—C31 | 1.7 (4) | N3—C4—C5—S1 | 3.5 (3) |
| C32—C29—C30—C31 | −178.5 (3) | C2—S1—C5—C6 | −179.9 (3) |
| C26—C31—C30—C29 | −0.9 (4) | C2—S1—C5—C4 | −1.2 (2) |
| C30—C29—C28—C27 | −1.0 (4) | C39—C38—C37—C36 | −1.7 (6) |
| C32—C29—C28—C27 | 179.2 (3) | C41—C36—C37—C38 | 0.0 (6) |
| N2—C19—C18—C17 | −56.4 (3) | N1—C36—C37—C38 | 177.4 (3) |
| C20—C17—C18—C19 | −176.0 (3) | C10—C9—C8—C7 | −1.4 (5) |
| C16—C17—C18—C19 | 55.8 (3) | C12—C7—C8—C9 | 0.9 (5) |
| C12—N2—C15—C16 | 157.4 (3) | C6—C7—C8—C9 | −175.5 (3) |
| C19—N2—C15—C16 | −59.9 (3) | C36—C41—C40—C39 | −0.7 (6) |
| C8—C7—C6—C5 | −38.0 (5) | C38—C39—C40—C41 | −0.8 (5) |
| C12—C7—C6—C5 | 145.6 (3) | C42—C39—C40—C41 | −179.7 (3) |

*Hydrogen-bond geometry (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N1—H1···O3 | 0.86 | 1.97 | 2.806 (4) | 164 |
| C8—H8···S1 | 0.93 | 2.68 | 3.224 (3) | 118 |
| C19—H19*B*···O2$^{i}$ | 0.97 | 2.53 | 3.398 (4) | 149 |
| C32—H32*A*···O3$^{ii}$ | 0.96 | 2.54 | 3.423 (5) | 152 |
| C37—H37···S2 | 0.93 | 2.58 | 3.210 (4) | 125 |

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