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# 4-(3-Fluoroanilino)thieno[2,3-*b*]pyridine-6-carboxylic acid

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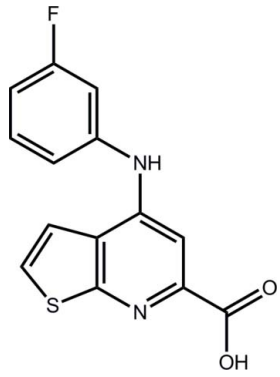
Key indicators: single-crystal X-ray study; $T$ = 120 K; mean $\sigma$(C–C) = 0.003 Å; disorder in main residue; $R$ factor = 0.035; $wR$ factor = 0.087; data-to-parameter ratio = 13.4.

In the title compound, $C_{14}H_9FN_2O_2S$, the thieno[2,3-*b*]pyridine residue is almost planar (r.m.s. deviation = 0.0194 Å), with the carboxylic acid group [dihedral angle = 11.9 (3)°] and the benzene ring [71.1 (4)°] being twisted out of this plane to different extents. An intramolecular N—H···O(carbonyl) hydrogen bond closes an $S$(6) ring. Supramolecular chains along [01$\bar{1}$] mediated by O—H···N(pyridine) hydrogen bonds feature in the crystal. A three-dimensional architecture is completed by $\pi$–$\pi$ interactions occurring between the benzene ring and the two rings of the thieno[2,3-*b*]pyridine residue [centroid–centroid distances = 3.6963 (13) and 3.3812 (13) Å]. The F atom is disordered over the two *meta* sites in a near statistical ratio [0.545 (5):0.455 (5)].

## Related literature

For the biological activity of 4-(arylamino)thieno[2,3-*b*]pyridine-5-carboxylic acids, see: Bernardino *et al.* (2007); Pinheiro *et al.* (2008). For the synthesis, see: Leal *et al.* (2008).




## Experimental

### Crystal data

$C_{14}H_9FN_2O_2S$
$M_r$ = 288.29
Orthorhombic, $Pna2_1$
$a$ = 17.0666 (6) Å
$b$ = 8.7147 (3) Å
$c$ = 7.9931 (2) Å
$V$ = 1188.82 (7) Å$^3$
$Z$ = 4
Mo $K\alpha$ radiation
$\mu$ = 0.29 mm$^{-1}$
$T$ = 120 K
0.66 × 0.24 × 0.17 mm

### Data collection

Bruker–Nonius Roper CCD camera on $\kappa$-goniostat diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2007)
$T_{min}$ = 0.788, $T_{max}$ = 1.000
10259 measured reflections
2643 independent reflections
2376 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.058

### Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.035
$wR(F^2)$ = 0.087
$S$ = 1.06
2643 reflections
197 parameters
3 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.20 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.42 e Å$^{-3}$
Absolute structure: Flack (1983), 1181 Friedel pairs
Flack parameter: 0.15 (9)

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| O1—H1o···N1$^{i}$ | 0.86 (2) | 1.84 (2) | 2.681 (2) | 167 (3) |
| N2—H2n···O2 | 0.88 (2) | 1.85 (2) | 2.635 (2) | 147 (2) |

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

Data collection: *COLLECT* (Hooft, 1998); cell refinement: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT*; data reduction: *DENZO* and *COLLECT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *DIAMOND* (Brandenburg, 2006); 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: HB6844).

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# supporting information

*Acta Cryst.* (2012). E**68**, o2217–o2218 [https://doi.org/10.1107/S1600536812027195]

## 4-(3-Fluoroanilino)thieno[2,3-*b*]pyridine-6-carboxylic acid

**Luiz C. S. Pinheiro, Alice M. R. Bernardino, Solange M. S. V. Wardell, James L. Wardell and Edward R. T. Tiekink**

### S1. Comment

Among the reported thienopyridine derivatives is a family of 4-(arylamino)thieno[2,3-*b*]pyridine-5-carboxylic acids, whose anti-virial and anti-bacterial activities have been investigated (Leal *et al.*, 2008; Bernardino *et al.*, 2007; Pinheiro *et al.*, 2008). The structure of one of these derivatives, the title compound (I), is now reported.

In (I), Fig. 1, the nine atoms comprising the thieno[2,3-*b*]pyridine fused ring system are planar with a r.m.s. deviation of 0.0194 Å and maximum deviations of 0.0343 (19) and -0.0227 (16) for the C7 and C6 atoms, respectively. The carboxylic acid residue is twisted out of this plane, forming a dihedral angle of 11.9 (3)°, and the terminal benzene ring, which is orientated towards the thienyl ring, is almost orthogonal, the dihedral angle being 71.1 (4)°. There is an intramolecular *N*—*H*···*O*(carbonyl) hydrogen bond, Table 1, which closes an *S*(6) loop.

In the crystal packing, supramolecular chains along [0 1 - 1] are formed *via* O—H···N(pyridyl) hydrogen bonds, Fig. 2 and Table 1. These are consolidated into a three-dimensional architecture *via* *π*—*π* interactions whereby the thieno[2,3-*b*]pyridine residue is straddled by a symmetry related benzene ring [inter-centroid (thienyl···benzene) distance = 3.6963 (13) Å, angle of inclination = 1.41 (12)°, and inter-centroid (pyridyl···benzene) distance = 3.3812 (13) Å and angle of inclination = 3.25 (11)° for symmetry operation -*x*, 2 - *y*, -1/2 + *z*], Fig. 3.

### S2. Experimental

The title compound was prepared as reported (Leal *et al.*, 2008). The dark orange blade used in the structure determination was grown from its toluene/acetonitrile solution.

### S3. Refinement

The C-bound H atoms were geometrically placed (C—H = 0.95 Å) and refined as riding with $U_{iso}$(H) = 1.2$U_{eq}$(C). The O– and N-bound H atoms were located from a difference map and refined with distance restraints of O—H = 0.84±0.01 and N—H = 0.88±0.01 Å, and with $U_{iso}$(H) = $zU_{eq}$(carrier atom); $z$ = 1.5 for O and $z$ = 1.2 for N. The F1 atom is disordered over two position. Each site was refined with individual anisotropic displacement parameters. The major component refined to a site occupancy factor = 0.545 (5). The $(02\bar{2})$ reflection was omitted from the final refinement owing to poor agreement.

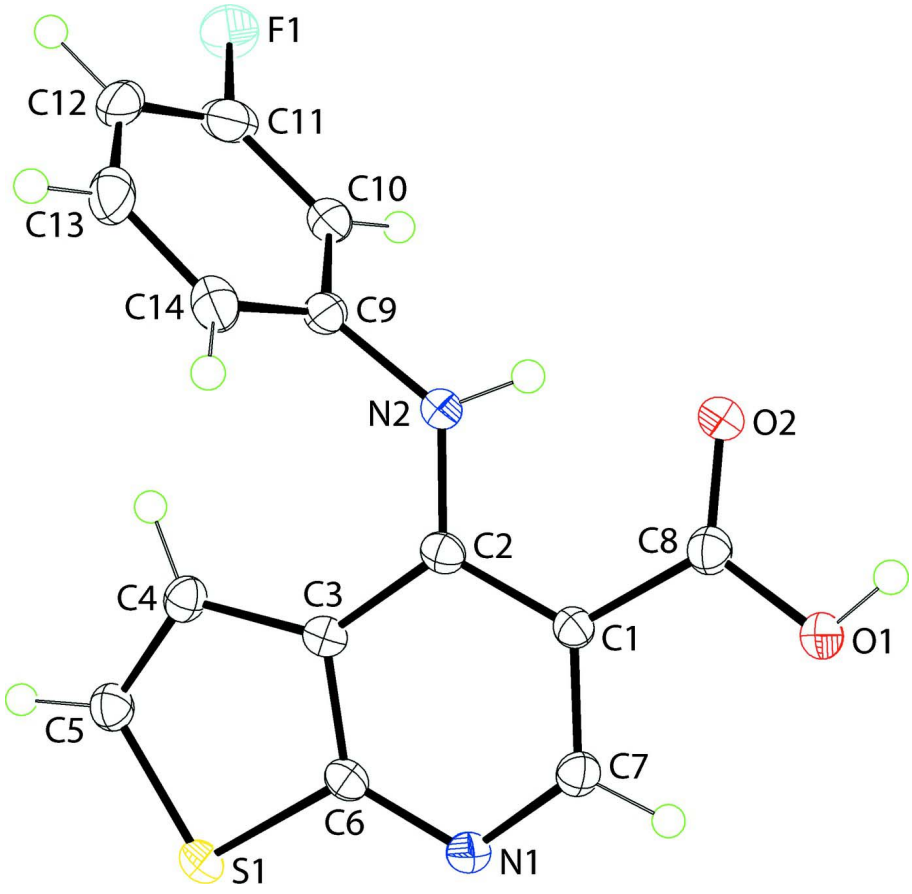


**Figure 1**

The molecular structure of (I) showing displacement ellipsoids at the 50% probability level.

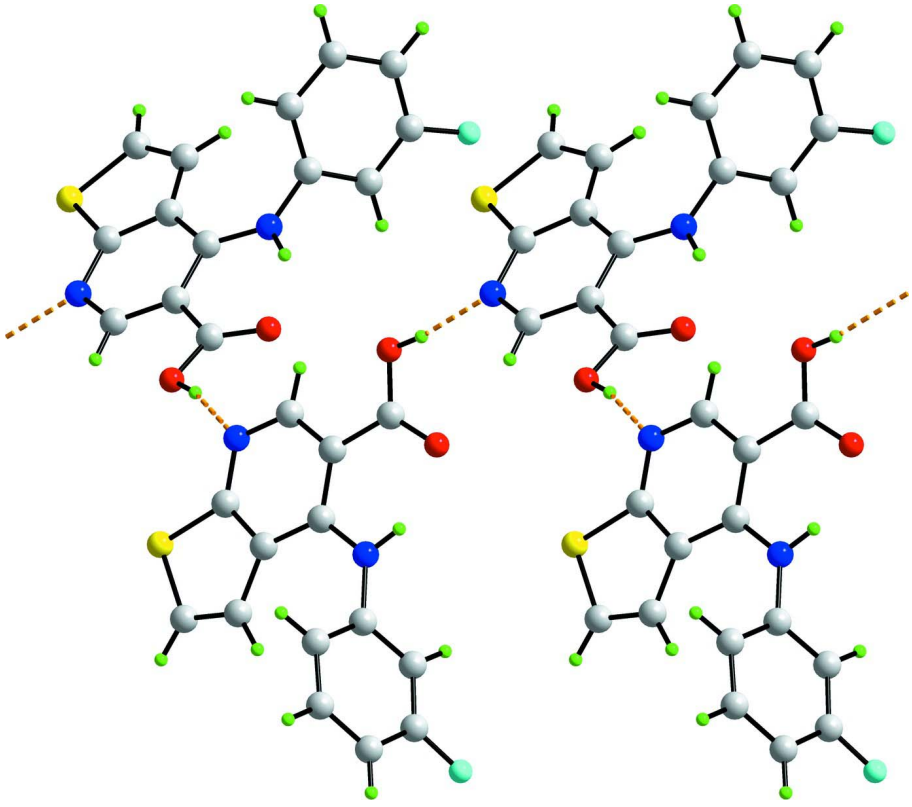

**Figure 2**

A view of the supramolecular chain in (I) sustained by O—H···N (orange dashed lines) hydrogen bonds.

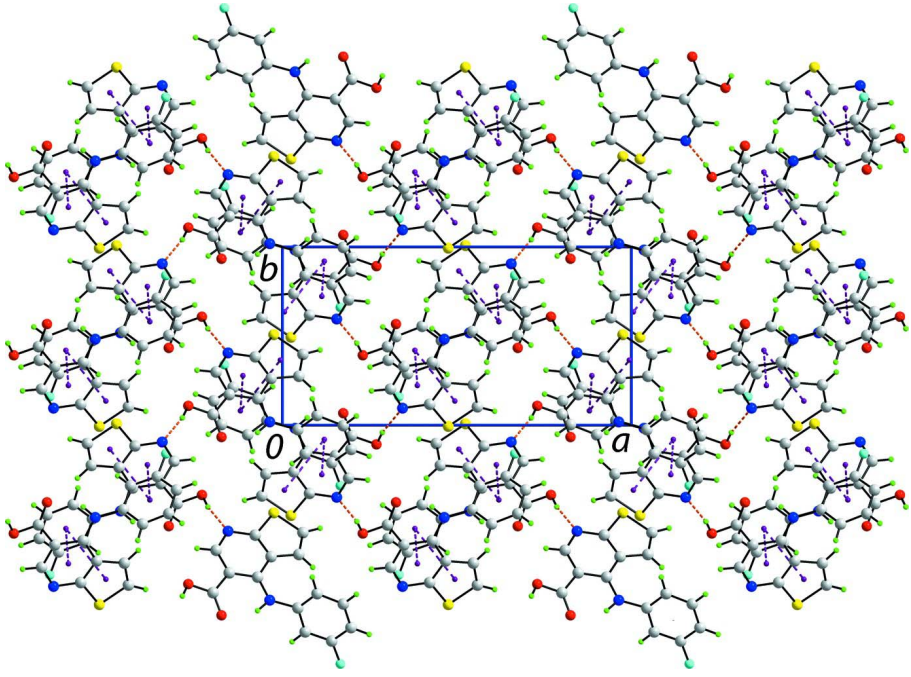


**Figure 3**

A view in projection down the *c* axis of the unit-cell contents for (I). The O—H···N and $\pi$—$\pi$ interactions are shown as orange and purple dashed lines, respectively.

## 4-(3-Fluoroanilino)thieno[2,3-*b*]pyridine-6-carboxylic acid

*Crystal data*

$C_{14}H_9FN_2O_2S$
$M_r = 288.29$
Orthorhombic, $Pna2_1$
Hall symbol: P 2c -2n
$a = 17.0666$ (6) Å
$b = 8.7147$ (3) Å
$c = 7.9931$ (2) Å
$V = 1188.82$ (7) Å$^3$
$Z = 4$
$F(000) = 592$
$D_x = 1.611$ Mg m$^{-3}$
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 1601 reflections
$\theta = 1.0$–$27.5°$
$\mu = 0.29$ mm$^{-1}$
$T = 120$ K
Blade, dark-orange
0.66 × 0.24 × 0.17 mm

*Data collection*

Bruker–Nonius Roper CCD camera on $\kappa$-goniostat diffractometer
Radiation source: Bruker-Nonius FR591 rotating anode
Graphite monochromator
Detector resolution: 9.091 pixels mm$^{-1}$
$\varphi$ & $\omega$ scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2007)
$T_{min} = 0.788$, $T_{max} = 1.000$
10259 measured reflections
2643 independent reflections
2376 reflections with $I > 2\sigma(I)$
$R_{int} = 0.058$
$\theta_{max} = 27.5°$, $\theta_{min} = 3.5°$
$h = -22 \rightarrow 22$
$k = -11 \rightarrow 11$
$l = -10 \rightarrow 9$

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.035$
$wR(F^2) = 0.087$
$S = 1.06$
2643 reflections
197 parameters
3 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
$w = 1/[\sigma^2(F_o^2) + (0.0375P)^2 + 0.2847P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.20$ e Å$^{-3}$
$\Delta\rho_{min} = -0.42$ e Å$^{-3}$
Absolute structure: Flack (1983), 1181 Friedel pairs
Absolute structure parameter: 0.15 (9)

*Special details*

**Geometry**. All s.u.'s (except the s.u. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell s.u.'s are taken into account individually in the estimation of s.u.'s in distances, angles and torsion angles; correlations between s.u.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell s.u.'s is used for estimating s.u.'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 $F^2 > 2\sigma(F^2)$ 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 | 0.02466 (3) | 0.49277 (6) | 0.56709 (9) | 0.02149 (14) | |
| O1 | 0.26956 (9) | 0.89190 (18) | 1.0209 (2) | 0.0246 (4) | |

| | | | | | |
|---|---|---|---|---|---|
| H1O | 0.2865 (16) | 0.959 (2) | 1.090 (3) | 0.037* | |
| O2 | 0.17443 (8) | 1.06688 (18) | 1.0208 (2) | 0.0254 (4) | |
| N1 | 0.15569 (10) | 0.5951 (2) | 0.7157 (2) | 0.0185 (4) | |
| N2 | 0.03616 (11) | 0.9821 (2) | 0.9068 (3) | 0.0214 (4) | |
| H2N | 0.0711 (11) | 1.041 (3) | 0.956 (3) | 0.026* | |
| C1 | 0.18990 (13) | 0.7023 (2) | 0.8094 (3) | 0.0184 (5) | |
| H1 | 0.2445 | 0.6918 | 0.8298 | 0.022* | |
| C2 | 0.15232 (12) | 0.8288 (2) | 0.8800 (2) | 0.0161 (4) | |
| C3 | 0.07089 (13) | 0.8526 (2) | 0.8490 (3) | 0.0167 (4) | |
| C4 | 0.03239 (12) | 0.7380 (2) | 0.7525 (3) | 0.0154 (4) | |
| C5 | −0.04725 (13) | 0.7259 (2) | 0.6927 (3) | 0.0190 (5) | |
| H5 | −0.0872 | 0.7977 | 0.7195 | 0.023* | |
| C6 | −0.05889 (12) | 0.6029 (2) | 0.5952 (3) | 0.0214 (5) | |
| H6 | −0.1081 | 0.5784 | 0.5464 | 0.026* | |
| C7 | 0.07779 (12) | 0.6170 (2) | 0.6923 (3) | 0.0172 (4) | |
| C8 | 0.19891 (12) | 0.9401 (3) | 0.9793 (3) | 0.0198 (5) | |
| C9 | −0.04436 (13) | 1.0256 (3) | 0.9067 (3) | 0.0197 (5) | |
| C10 | −0.06524 (14) | 1.1599 (3) | 0.8256 (3) | 0.0222 (5) | |
| H10 | −0.0279 | 1.2153 | 0.7613 | 0.027* | |
| C12 | −0.19667 (14) | 1.1360 (3) | 0.9319 (4) | 0.0341 (6) | |
| H12 | −0.2487 | 1.1741 | 0.9406 | 0.041* | |
| C14 | −0.09947 (13) | 0.9457 (3) | 1.0002 (3) | 0.0245 (5) | |
| H14 | −0.0857 | 0.8531 | 1.0554 | 0.029* | |
| C11 | −0.14136 (15) | 1.2115 (3) | 0.8400 (3) | 0.0315 (6) | 0.545 (5) |
| C13 | −0.17454 (14) | 1.0032 (3) | 1.0113 (3) | 0.0310 (6) | 0.545 (5) |
| H13 | −0.2122 | 0.9491 | 1.0761 | 0.037* | 0.545 (5) |
| F1 | −0.16627 (15) | 1.3395 (3) | 0.7761 (3) | 0.0330 (9) | 0.545 (5) |
| C11′ | −0.14136 (15) | 1.2115 (3) | 0.8400 (3) | 0.0315 (6) | 0.455 (5) |
| H11 | −0.1559 | 1.3032 | 0.7838 | 0.038* | 0.455 (5) |
| C13′ | −0.17454 (14) | 1.0032 (3) | 1.0113 (3) | 0.0310 (6) | 0.455 (5) |
| F1′ | −0.23113 (18) | 0.9534 (4) | 1.1023 (4) | 0.0392 (12) | 0.455 (5) |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| S1 | 0.0221 (2) | 0.0178 (2) | 0.0245 (3) | −0.0018 (2) | −0.0014 (3) | −0.0059 (2) |
| O1 | 0.0187 (7) | 0.0219 (8) | 0.0332 (9) | 0.0019 (6) | −0.0077 (6) | −0.0077 (7) |
| O2 | 0.0198 (8) | 0.0194 (8) | 0.0370 (10) | −0.0001 (6) | −0.0014 (7) | −0.0092 (7) |
| N1 | 0.0181 (9) | 0.0169 (9) | 0.0205 (9) | 0.0010 (7) | 0.0011 (7) | −0.0018 (8) |
| N2 | 0.0165 (9) | 0.0178 (9) | 0.0300 (11) | 0.0007 (7) | −0.0026 (8) | −0.0070 (8) |
| C1 | 0.0175 (10) | 0.0170 (10) | 0.0208 (12) | 0.0006 (8) | −0.0013 (8) | 0.0037 (9) |
| C2 | 0.0162 (10) | 0.0149 (9) | 0.0171 (11) | −0.0008 (8) | −0.0004 (8) | −0.0001 (8) |
| C3 | 0.0198 (11) | 0.0139 (10) | 0.0163 (10) | −0.0010 (8) | 0.0016 (8) | 0.0019 (9) |
| C4 | 0.0194 (10) | 0.0147 (10) | 0.0123 (10) | 0.0002 (8) | 0.0006 (8) | 0.0015 (8) |
| C5 | 0.0172 (10) | 0.0201 (11) | 0.0197 (11) | 0.0003 (8) | −0.0007 (8) | 0.0030 (9) |
| C6 | 0.0203 (10) | 0.0213 (10) | 0.0226 (12) | −0.0011 (8) | −0.0030 (9) | −0.0002 (9) |
| C7 | 0.0204 (10) | 0.0145 (10) | 0.0165 (10) | −0.0013 (8) | 0.0003 (8) | 0.0006 (8) |
| C8 | 0.0184 (11) | 0.0211 (11) | 0.0199 (12) | −0.0006 (9) | −0.0015 (9) | −0.0005 (9) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C9 | 0.0178 (10) | 0.0219 (11) | 0.0194 (11) | 0.0016 (9) | −0.0033 (8) | −0.0071 (9) |
| C10 | 0.0214 (12) | 0.0197 (11) | 0.0256 (12) | −0.0001 (10) | −0.0029 (9) | −0.0040 (10) |
| C12 | 0.0170 (11) | 0.0419 (15) | 0.0434 (15) | 0.0045 (11) | −0.0050 (11) | −0.0252 (13) |
| C14 | 0.0249 (12) | 0.0257 (11) | 0.0230 (12) | −0.0059 (10) | 0.0003 (10) | −0.0021 (10) |
| C11 | 0.0325 (14) | 0.0242 (12) | 0.0379 (15) | 0.0084 (11) | −0.0111 (12) | −0.0113 (11) |
| C13 | 0.0208 (12) | 0.0425 (16) | 0.0296 (14) | −0.0062 (10) | 0.0022 (10) | −0.0162 (12) |
| F1 | 0.0327 (16) | 0.0212 (14) | 0.0452 (18) | 0.0071 (12) | −0.0064 (12) | 0.0067 (12) |
| C11′ | 0.0325 (14) | 0.0242 (12) | 0.0379 (15) | 0.0084 (11) | −0.0111 (12) | −0.0113 (11) |
| C13′ | 0.0208 (12) | 0.0425 (16) | 0.0296 (14) | −0.0062 (10) | 0.0022 (10) | −0.0162 (12) |
| F1′ | 0.0281 (18) | 0.046 (2) | 0.044 (2) | −0.0163 (14) | 0.0099 (15) | −0.0147 (18) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| S1—C7 | 1.731 (2) | C6—H6 | 0.9500 |
| S1—C6 | 1.733 (2) | C9—C14 | 1.388 (3) |
| O1—C8 | 1.319 (3) | C9—C10 | 1.384 (3) |
| O1—H1O | 0.852 (10) | C10—C11′ | 1.380 (3) |
| O2—C8 | 1.227 (3) | C10—C11 | 1.380 (3) |
| N1—C1 | 1.332 (3) | C10—H10 | 0.9500 |
| N1—C7 | 1.356 (3) | C12—C11′ | 1.365 (4) |
| N2—C3 | 1.356 (3) | C12—C11 | 1.365 (4) |
| N2—C9 | 1.426 (3) | C12—C13′ | 1.373 (4) |
| N2—H2N | 0.881 (10) | C12—C13 | 1.373 (4) |
| C1—C2 | 1.394 (3) | C12—H12 | 0.9500 |
| C1—H1 | 0.9500 | C14—C13′ | 1.378 (3) |
| C2—C3 | 1.427 (3) | C14—C13 | 1.378 (3) |
| C2—C8 | 1.484 (3) | C14—H14 | 0.9500 |
| C3—C4 | 1.422 (3) | C11—F1 | 1.298 (4) |
| C4—C7 | 1.394 (3) | C13—H13 | 0.9500 |
| C4—C5 | 1.445 (3) | C11′—H11 | 0.9500 |
| C5—C6 | 1.340 (3) | C13′—F1′ | 1.284 (4) |
| C5—H5 | 0.9500 | | |

| | | | |
|---|---|---|---|
| C7—S1—C6 | 90.55 (10) | C11′—C10—C9 | 118.6 (2) |
| C8—O1—H1O | 104.9 (19) | C11—C10—C9 | 118.6 (2) |
| C1—N1—C7 | 114.12 (18) | C11′—C10—H10 | 120.7 |
| C3—N2—C9 | 129.99 (18) | C11—C10—H10 | 120.7 |
| C3—N2—H2N | 110.0 (17) | C9—C10—H10 | 120.7 |
| C9—N2—H2N | 119.9 (17) | C11′—C12—C11 | 0.0 (3) |
| N1—C1—C2 | 125.5 (2) | C11′—C12—C13′ | 117.7 (2) |
| N1—C1—H1 | 117.3 | C11—C12—C13′ | 117.7 (2) |
| C2—C1—H1 | 117.3 | C11′—C12—C13 | 117.7 (2) |
| C1—C2—C3 | 119.5 (2) | C11—C12—C13 | 117.7 (2) |
| C1—C2—C8 | 119.12 (19) | C13′—C12—C13 | 0.0 (2) |
| C3—C2—C8 | 121.30 (19) | C11′—C12—H12 | 121.1 |
| N2—C3—C4 | 124.5 (2) | C11—C12—H12 | 121.1 |
| N2—C3—C2 | 119.2 (2) | C13′—C12—H12 | 121.1 |
| C4—C3—C2 | 116.25 (18) | C13—C12—H12 | 121.1 |

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| C7—C4—C3 | 117.46 (18) | C9—C14—C13′ | 118.9 (2) |
| C7—C4—C5 | 110.70 (19) | C9—C14—C13 | 118.9 (2) |
| C3—C4—C5 | 131.71 (19) | C13′—C14—C13 | 0.00 (7) |
| C6—C5—C4 | 113.0 (2) | C9—C14—H14 | 120.6 |
| C6—C5—H5 | 123.5 | C13′—C14—H14 | 120.6 |
| C4—C5—H5 | 123.5 | C13—C14—H14 | 120.6 |
| C5—C6—S1 | 113.36 (17) | F1—C11—C12 | 113.5 (3) |
| C5—C6—H6 | 123.3 | F1—C11—C10 | 123.8 (3) |
| S1—C6—H6 | 123.3 | C12—C11—C10 | 122.6 (2) |
| N1—C7—C4 | 127.12 (19) | C12—C13—C14 | 122.1 (2) |
| N1—C7—S1 | 120.36 (16) | C12—C13—H13 | 118.9 |
| C4—C7—S1 | 112.43 (15) | C14—C13—H13 | 118.9 |
| O2—C8—O1 | 122.0 (2) | C12—C11′—C10 | 122.6 (2) |
| O2—C8—C2 | 123.44 (19) | C12—C11′—H11 | 118.7 |
| O1—C8—C2 | 114.57 (19) | C10—C11′—H11 | 118.7 |
| C14—C9—C10 | 120.1 (2) | F1′—C13′—C12 | 109.9 (3) |
| C14—C9—N2 | 121.3 (2) | F1′—C13′—C14 | 127.8 (3) |
| C10—C9—N2 | 118.2 (2) | C12—C13′—C14 | 122.1 (2) |
| C11′—C10—C11 | 0.0 (2) | | |

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| C7—N1—C1—C2 | −0.3 (3) | C10—C9—C14—C13′ | −0.5 (3) |
| N1—C1—C2—C3 | −1.9 (3) | N2—C9—C14—C13′ | 172.4 (2) |
| N1—C1—C2—C8 | −178.91 (19) | C10—C9—C14—C13 | −0.5 (3) |
| C9—N2—C3—C4 | 9.1 (4) | N2—C9—C14—C13 | 172.4 (2) |
| C9—N2—C3—C2 | −173.2 (2) | C11′—C12—C11—F1 | 0 (97) |
| C1—C2—C3—N2 | −174.7 (2) | C13′—C12—C11—F1 | −176.8 (2) |
| C8—C2—C3—N2 | 2.2 (3) | C13—C12—C11—F1 | −176.8 (2) |
| C1—C2—C3—C4 | 3.1 (3) | C11′—C12—C11—C10 | 0 (100) |
| C8—C2—C3—C4 | −179.95 (19) | C13′—C12—C11—C10 | −0.4 (4) |
| N2—C3—C4—C7 | 175.4 (2) | C13—C12—C11—C10 | −0.4 (4) |
| C2—C3—C4—C7 | −2.3 (3) | C11′—C10—C11—F1 | 0 (100) |
| N2—C3—C4—C5 | 0.0 (4) | C9—C10—C11—F1 | 176.5 (3) |
| C2—C3—C4—C5 | −177.7 (2) | C11′—C10—C11—C12 | 0 (75) |
| C7—C4—C5—C6 | 0.2 (3) | C9—C10—C11—C12 | 0.4 (4) |
| C3—C4—C5—C6 | 175.9 (2) | C11′—C12—C13—C14 | −0.1 (4) |
| C4—C5—C6—S1 | −0.3 (3) | C11—C12—C13—C14 | −0.1 (4) |
| C7—S1—C6—C5 | 0.20 (18) | C13′—C12—C13—C14 | 0 (100) |
| C1—N1—C7—C4 | 1.2 (3) | C9—C14—C13—C12 | 0.6 (4) |
| C1—N1—C7—S1 | 177.51 (16) | C13′—C14—C13—C12 | 0 (100) |
| C3—C4—C7—N1 | 0.2 (3) | C11—C12—C11′—C10 | 0 (100) |
| C5—C4—C7—N1 | 176.5 (2) | C13′—C12—C11′—C10 | −0.4 (4) |
| C3—C4—C7—S1 | −176.41 (16) | C13—C12—C11′—C10 | −0.4 (4) |
| C5—C4—C7—S1 | −0.1 (2) | C11—C10—C11′—C12 | 0 (75) |
| C6—S1—C7—N1 | −176.90 (18) | C9—C10—C11′—C12 | 0.4 (4) |
| C6—S1—C7—C4 | −0.07 (17) | C11′—C12—C13′—F1′ | 174.9 (3) |
| C1—C2—C8—O2 | 166.8 (2) | C11—C12—C13′—F1′ | 174.9 (3) |
| C3—C2—C8—O2 | −10.2 (3) | C13—C12—C13′—F1′ | 0 (59) |
| C1—C2—C8—O1 | −13.5 (3) | C11′—C12—C13′—C14 | −0.1 (4) |

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| C3—C2—C8—O1 | 169.52 (19) | C11—C12—C13′—C14 | −0.1 (4) |
| C3—N2—C9—C14 | 65.4 (4) | C13—C12—C13′—C14 | 0 (100) |
| C3—N2—C9—C10 | −121.5 (3) | C9—C14—C13′—F1′ | −173.6 (3) |
| C14—C9—C10—C11′ | 0.0 (3) | C13—C14—C13′—F1′ | 0 (79) |
| N2—C9—C10—C11′ | −173.1 (2) | C9—C14—C13′—C12 | 0.6 (4) |
| C14—C9—C10—C11 | 0.0 (3) | C13—C14—C13′—C12 | 0 (100) |
| N2—C9—C10—C11 | −173.1 (2) | | |

*Hydrogen-bond geometry (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| O1—H1o···N1$^{i}$ | 0.86 (2) | 1.84 (2) | 2.681 (2) | 167 (3) |
| N2—H2n···O2 | 0.88 (2) | 1.85 (2) | 2.635 (2) | 147 (2) |

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