IUCrData

ISSN 2414-3146

# Ethyl 4-(2,5-dimethylphenyl)-6-methyl-2-sulfanylidene-1,2,3,4-tetrahydropyrimidine-5-carboxylate

**Shashi R and Noor Shahina Begum***

Department of Studies in Chemistry, Central College Campus, Bangalore University, Bangalore 560 001, Karnataka, India. *Correspondence e-mail: noorsb@rediffmail.com

Received 6 September 2017
Accepted 6 October 2017

Edited by W. T. A. Harrison, University of Aberdeen, Scotland

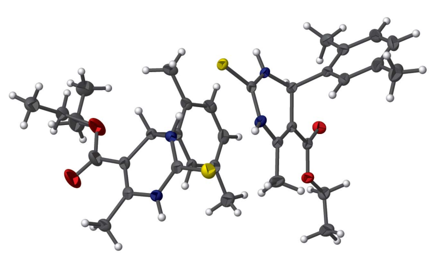
**Keywords:** crystal structure; DHPM derivative; hydrogen bonding.

**CCDC reference**: 1578486

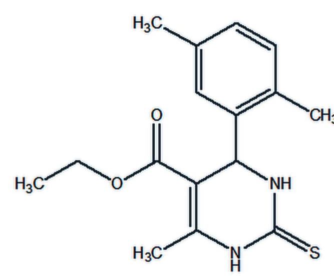
**Structural data**: full structural data are available from iucrdata.iucr.org

The title compound, $C_{16}H_{20}N_2O_2S$, crystallizes with two molecules in the asymmetric unit, one of which shows positional disorder of the ethyl side chain over two orientations in a 0.555 (7):0.445 (7) ratio. The hydropyrimidine ring adopts a shallow *boat* conformation and the 2,5-dimethylphenyl ring is positioned axially. The crystal structure features N—H···S, N—H···O and C—H···O hydrogen bonds, which link the molecules into $(10\overline{1})$ sheets.

**3D view**



**Chemical scheme**




## Structure description

Dihydropyrimidine (DHPM) derivatives are used as calcium channel blockers (Zorkun *et al.*, 2006) and inhibitors of mitotic kinesin Eg5 for treating cancer (Cochran *et al.*, 2005). As part of our studies of DHPM derivatives, the title compound, $C_{14}H_{14}F_4N_2O_3S$, was isolated and the structure determined by X-ray diffraction. The molecular structure of the compound is shown in Fig. 1. The title compound crystallizes with two molecules (*A* and *B*) in the asymmetric unit. The 2,5-dimethyl phenyl ring subtends dihedral angles with the pyrimidine ring of 88.7 (1) and 88.75 (1)° for *A* and *B*, respectively. The pyrimidine ring adopts a boat conformation with atoms N2 and C6 displaced by 0.130 (3) and 0.279 (8) Å, respectively, from the mean plane of the other four atoms (C2/C4/C5/N1) in molecule *A*. Similarly, the pyrimidine ring of molecule *B* adopts a boat conformation with atoms N2′ and C6′ displaced by 0.110 (4) and 0.325 (8) Å, respectively, from the mean plane of the other four atoms (C2′/C4′/C5′/N1′).

The crystal structure features N—H···S, N–H···O and C—H···O hydrogen bonds (Table 1), which link the molecules into $(10\overline{1})$ sheets incorporating $R_2^2(8)$ loops (Fig. 2).

## Synthesis and crystallization

A mixture of 2,5-dimethylbenzaldehydes (10 mmol), thiourea (10 mmol), ethyl acetoacetate (10 mmol) and a catalytic amount of concentrated hydrochloric acid in ethanol

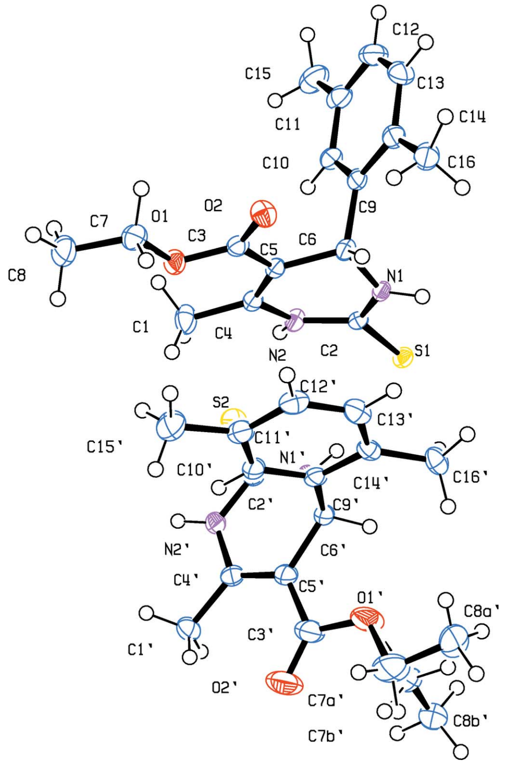



**Figure 1**
The molecular structure of the title compound, with displacement ellipsoids drawn at the 50% probability level.

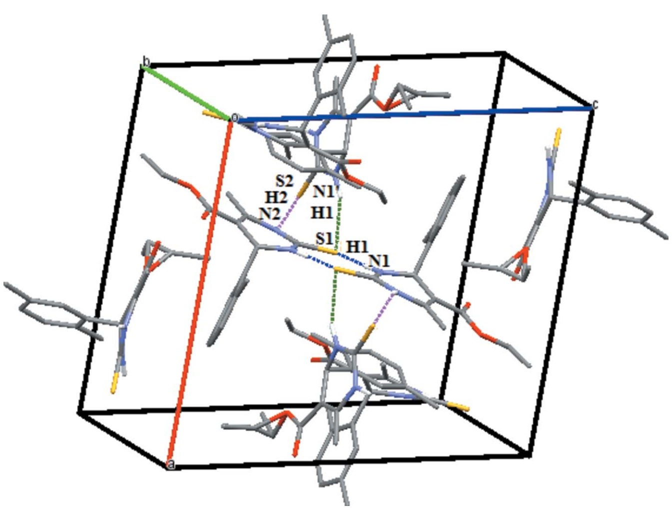



**Figure 2**
Unit-cell packing of the title compound, showing N2—H2···S2 and N1—H1···S1 interactions as dotted lines. H atoms not involved in hydrogen bonding have been excluded.

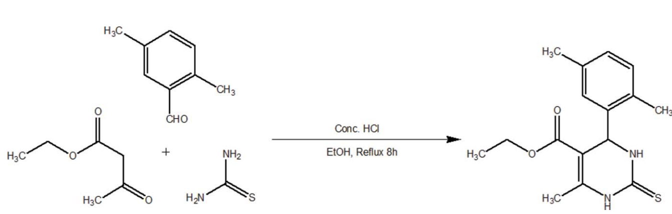



**Figure 3**
The reaction scheme for the preparation of the title compound.

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

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N1—H1···S1$^{i}$ | 0.88 | 2.47 | 3.315 (2) | 160 |
| N1′—H1′···S1 | 0.88 | 2.49 | 3.316 (2) | 156 |
| N2—H2···S2 | 0.88 | 2.65 | 3.431 (2) | 148 |
| N2′—H2′···O2$^{ii}$ | 0.88 | 1.97 | 2.833 (3) | 168 |
| C1—H1*C*···O2′$^{iii}$ | 0.98 | 2.58 | 3.477 (5) | 152 |
| C1′—H1′2···O2$^{ii}$ | 0.98 | 2.56 | 3.377 (4) | 141 |
| C16—H16*A*···S1$^{i}$ | 0.98 | 2.77 | 3.717 (3) | 162 |

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

**Table 2**
Experimental details.

| | |
|---|---|
| Crystal data | |
| Chemical formula | $C_{16}H_{20}N_2O_2S$ |
| $M_r$ | 304.40 |
| Crystal system, space group | Monoclinic, $P2_1/n$ |
| Temperature (K) | 100 |
| *a*, *b*, *c* (Å) | 14.4124 (7), 14.9172 (6), 15.1412 (6) |
| β (°) | 100.377 (1) |
| *V* (Å$^3$) | 3202.0 (2) |
| *Z* | 8 |
| Radiation type | Mo *K*α |
| μ (mm$^{-1}$) | 0.21 |
| Crystal size (mm) | 0.15 × 0.15 × 0.14 |
| | |
| Data collection | |
| Diffractometer | Bruker SMART APEX CCD |
| Absorption correction | Multi-scan (*SADABS*; Bruker, 1998) |
| $T_{min}$, $T_{max}$ | 0.969, 0.971 |
| No. of measured, independent and observed [$I > 2\sigma(I)$] reflections | 25239, 5637, 4227 |
| $R_{int}$ | 0.049 |
| $(\sin \theta/\lambda)_{max}$ (Å$^{-1}$) | 0.595 |
| | |
| Refinement | |
| $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S* | 0.049, 0.146, 0.78 |
| No. of reflections | 5637 |
| No. of parameters | 407 |
| H-atom treatment | H-atom parameters constrained |
| $\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å$^{-3}$) | 0.51, −0.34 |

Computer programs: *SMART* and *SAINT-Plus* (Bruker, 1998), *SHELXS97* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2015) and *CAMERON* (Watkin *et al.*, 1996).

(20 ml) was refluxed for 8 h (Fig. 3). The reaction mixture was allowed to stand overnight at room temperature. The solid thus separated was neutralized by using aqueous sodium carbonate solution and the obtained precipitate was filtered and washed with a mixture of ethanol and water (1:1) and recrystallized from *N*,*N*-dimethylformamide solution yielding pale-yellow blocks of the title compound (Yield: 84%; m.p. 423–425 K) IR (KBr) ν cm$^{-1}$: 3298, 3174 (NH), 2982 (CH), 1702 (C═O), 1596 (C═C), 1567 (C═N). $^{1}$H NMR (500 MHz, DMSO-$d_6$) *d*: 8.95 (*s*, 1H), 8.05 (*s*, 1H), 6.80–6.90 (*m*, 3H), 5.45 (*s*, 1H), 3.85 (*q*, 2H), 2.30 (*s*, 6H), 2.20 (*s*, 3H), 0.97 (*t*, 3*H*). Mass (*m*/*z*): 304 *M*, 305 $M^{+}$, 199 (base peak), 231, 171.

## Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

## References

Bruker. (1998). *SMART*, *SAINT-Plus* and *SADABS.* Bruker AXS Inc., Madison, Wisconsin, USA.

Cochran, J. C., Gatial, J. E., Kapoor, T. M. & Gilbert, S. P. (2005). *J. Biol. Chem.* **280**, 12658–12667.

Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

Sheldrick, G. M. (2015). *Acta Cryst.* C**71**, 3–8.

Watkin, D. J., Prout, C. K. & Pearce, L. J. (1996). *CAMERON.* Chemical Crystallography Laboratory, University of Oxford, England.

Zorkun, I. S., İnci, S., Saraç, S., Çelebi, S. & Erol, K. (2006). *Bioorg. Med. Chem.* **14**, 8582–8589.

# full crystallographic data

*IUCrData* (2017). **2**, x171440 [https://doi.org/10.1107/S2414314617014407]

## Ethyl 4-(2,5-dimethylphenyl)-6-methyl-2-sulfanylidene-1,2,3,4-tetrahydro-pyrimidine-5-carboxylate

**Shashi R and Noor Shahina Begum**

### Ethyl 4-(2,5-dimethylphenyl)-6-methyl-2-sulfanylidene-1,2,3,4-tetrahydropyrimidine-5-carboxylate

*Crystal data*

$C_{16}H_{20}N_2O_2S$
$M_r$ = 304.40
Monoclinic, $P2_1/n$
$a$ = 14.4124 (7) Å
$b$ = 14.9172 (6) Å
$c$ = 15.1412 (6) Å
$\beta$ = 100.377 (1)°
$V$ = 3202.0 (2) Å$^3$
$Z$ = 8
$F(000)$ = 1296
$D_x$ = 1.263 Mg m$^{-3}$
Mo $K\alpha$ radiation, $\lambda$ = 0.71073 Å
Cell parameters from 5637 reflections
$\theta$ = 2.0–25.0°
$\mu$ = 0.21 mm$^{-1}$
$T$ = 100 K
Block, pale yellow
0.15 × 0.15 × 0.14 mm

*Data collection*

Bruker SMART APEX CCD diffractometer
$\omega$ scans
Absorption correction: multi-scan (SADABS; Bruker, 1998)
$T_{min}$ = 0.969, $T_{max}$ = 0.971
25239 measured reflections
5637 independent reflections
4227 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.049
$\theta_{max}$ = 25.0°, $\theta_{min}$ = 2.0°
$h$ = −17→17
$k$ = −17→17
$l$ = −17→18

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.049
$wR(F^2)$ = 0.146
$S$ = 0.78
5637 reflections
407 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.090P)^2 + 7.9246P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.51 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.34 e Å$^{-3}$

*Special details*

**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.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)*

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ | Occ. (<1) |
|---|---|---|---|---|---|
| S1 | 0.00143 (5) | 0.85136 (5) | 0.03650 (4) | 0.02149 (19) | |
| S2 | −0.12626 (5) | 0.60299 (5) | −0.02637 (5) | 0.0300 (2) | |
| O1 | −0.20098 (14) | 0.83962 (13) | −0.39604 (12) | 0.0256 (5) | |
| O2 | −0.13530 (14) | 0.97632 (13) | −0.38361 (13) | 0.0271 (5) | |
| N2′ | −0.30632 (16) | 0.63422 (15) | −0.01800 (16) | 0.0237 (5) | |
| H2′ | −0.3173 | 0.5816 | −0.0440 | 0.028* | |
| N1 | −0.02760 (15) | 0.94157 (15) | −0.11651 (14) | 0.0194 (5) | |
| H1 | −0.0160 | 0.9892 | −0.0821 | 0.023* | |
| N2 | −0.06218 (16) | 0.79254 (15) | −0.12882 (14) | 0.0211 (5) | |
| H2 | −0.0544 | 0.7385 | −0.1053 | 0.025* | |
| C2 | −0.03058 (18) | 0.86416 (18) | −0.07630 (18) | 0.0190 (6) | |
| C5 | −0.10039 (19) | 0.87969 (18) | −0.26024 (18) | 0.0196 (6) | |
| N1′ | −0.20635 (16) | 0.75143 (15) | 0.02123 (15) | 0.0235 (5) | |
| H1′ | −0.1486 | 0.7701 | 0.0420 | 0.028* | |
| C4 | −0.10644 (19) | 0.80106 (18) | −0.21849 (18) | 0.0224 (6) | |
| C6 | −0.04177 (19) | 0.95575 (18) | −0.21342 (17) | 0.0196 (6) | |
| H6 | −0.0778 | 1.0128 | −0.2276 | 0.024* | |
| C6′ | −0.2839 (2) | 0.81632 (19) | 0.02050 (19) | 0.0242 (6) | |
| H6′ | −0.2666 | 0.8567 | 0.0736 | 0.029* | |
| C14′ | −0.25847 (19) | 0.96154 (18) | −0.0615 (2) | 0.0224 (6) | |
| C1′ | −0.4641 (2) | 0.6189 (2) | 0.0127 (2) | 0.0292 (7) | |
| H1′1 | −0.4559 | 0.5894 | 0.0715 | 0.044* | |
| H1′2 | −0.4688 | 0.5734 | −0.0346 | 0.044* | |
| H1′3 | −0.5219 | 0.6549 | 0.0037 | 0.044* | |
| C3 | −0.14684 (19) | 0.90319 (18) | −0.35165 (18) | 0.0214 (6) | |
| C10′ | −0.3412 (2) | 0.8390 (2) | −0.1455 (2) | 0.0293 (7) | |
| H10′ | −0.3662 | 0.7800 | −0.1464 | 0.035* | |
| O1′ | −0.41751 (19) | 0.89949 (17) | 0.0866 (2) | 0.0715 (10) | |
| C5′ | −0.3723 (2) | 0.76588 (19) | 0.03087 (19) | 0.0266 (7) | |
| C11 | 0.1992 (2) | 0.8927 (2) | −0.2667 (2) | 0.0312 (7) | |
| C9′ | −0.29503 (19) | 0.87409 (18) | −0.0645 (2) | 0.0232 (6) | |
| C9 | 0.0534 (2) | 0.96553 (19) | −0.24365 (18) | 0.0224 (6) | |
| C10 | 0.1109 (2) | 0.8900 (2) | −0.24104 (18) | 0.0246 (6) | |
| H10 | 0.0892 | 0.8348 | −0.2211 | 0.030* | |
| C16′ | −0.2128 (2) | 1.00512 (19) | 0.0250 (2) | 0.0286 (7) | |
| H2′1 | −0.1864 | 1.0632 | 0.0121 | 0.043* | |
| H2′2 | −0.1623 | 0.9665 | 0.0560 | 0.043* | |
| H2′3 | −0.2601 | 1.0141 | 0.0633 | 0.043* | |
| C2′ | −0.2169 (2) | 0.66710 (19) | −0.00703 (18) | 0.0238 (6) | |
| C4′ | −0.3815 (2) | 0.6781 (2) | 0.00902 (18) | 0.0244 (6) | |
| C7 | −0.2443 (2) | 0.8619 (2) | −0.48809 (19) | 0.0302 (7) | |
| H7A | −0.1962 | 0.8847 | −0.5216 | 0.036* | |
| H7B | −0.2932 | 0.9086 | −0.4885 | 0.036* | |
| C1 | −0.1571 (2) | 0.7181 (2) | −0.2567 (2) | 0.0331 (7) | |
| H1A | −0.2253 | 0.7288 | −0.2671 | 0.050* | |

| | | | | | |
|---|---|---|---|---|---|
| H1B | −0.1415 | 0.6684 | −0.2143 | 0.050* | |
| H1C | −0.1377 | 0.7029 | −0.3136 | 0.050* | |
| C16 | 0.0274 (2) | 1.1324 (2) | −0.2750 (2) | 0.0333 (7) | |
| H16A | 0.0249 | 1.1514 | −0.2135 | 0.050* | |
| H16B | −0.0367 | 1.1215 | −0.3076 | 0.050* | |
| H16C | 0.0570 | 1.1797 | −0.3054 | 0.050* | |
| C12′ | −0.3134 (2) | 0.9720 (2) | −0.2225 (2) | 0.0290 (7) | |
| H12′ | −0.3183 | 1.0060 | −0.2762 | 0.035* | |
| C14 | 0.0843 (2) | 1.0479 (2) | −0.27263 (19) | 0.0272 (7) | |
| C13 | 0.1725 (2) | 1.0494 (2) | −0.2994 (2) | 0.0348 (8) | |
| H13 | 0.1948 | 1.1043 | −0.3197 | 0.042* | |
| O2′ | −0.5221 (2) | 0.78754 (19) | 0.0748 (3) | 0.0772 (11) | |
| C11′ | −0.3520 (2) | 0.8869 (2) | −0.2253 (2) | 0.0304 (7) | |
| C13′ | −0.2677 (2) | 1.0080 (2) | −0.1422 (2) | 0.0290 (7) | |
| H13′ | −0.2418 | 1.0665 | −0.1422 | 0.035* | |
| C8 | −0.2873 (3) | 0.7777 (2) | −0.5298 (2) | 0.0446 (9) | |
| H8A | −0.2381 | 0.7322 | −0.5288 | 0.067* | |
| H8B | −0.3174 | 0.7896 | −0.5920 | 0.067* | |
| H8C | −0.3347 | 0.7560 | −0.4959 | 0.067* | |
| C15′ | −0.4070 (3) | 0.8492 (2) | −0.3117 (2) | 0.0433 (9) | |
| H3′1 | −0.4013 | 0.8895 | −0.3615 | 0.065* | |
| H3′2 | −0.4736 | 0.8435 | −0.3067 | 0.065* | |
| H3′3 | −0.3819 | 0.7901 | −0.3230 | 0.065* | |
| C15 | 0.2608 (2) | 0.8103 (3) | −0.2595 (2) | 0.0421 (9) | |
| H15A | 0.2970 | 0.8056 | −0.1983 | 0.063* | |
| H15B | 0.3043 | 0.8149 | −0.3021 | 0.063* | |
| H15C | 0.2212 | 0.7570 | −0.2732 | 0.063* | |
| C12 | 0.2280 (2) | 0.9737 (2) | −0.2972 (2) | 0.0366 (8) | |
| H12 | 0.2868 | 0.9772 | −0.3170 | 0.044* | |
| C3′ | −0.4458 (3) | 0.8152 (2) | 0.0651 (3) | 0.0499 (10) | |
| C7A′ | −0.4956 (5) | 0.9670 (5) | 0.0962 (8) | 0.059 (2) | 0.555 (7) |
| H7A1 | −0.5440 | 0.9687 | 0.0408 | 0.071* | 0.555 (7) |
| H7A2 | −0.5264 | 0.9508 | 0.1474 | 0.071* | 0.555 (7) |
| C8A′ | −0.4474 (4) | 1.0547 (4) | 0.1120 (5) | 0.050 (2) | 0.555 (7) |
| H8A1 | −0.3936 | 1.0492 | 0.1615 | 0.075* | 0.555 (7) |
| H8A2 | −0.4917 | 1.0994 | 0.1274 | 0.075* | 0.555 (7) |
| H8A3 | −0.4251 | 1.0735 | 0.0575 | 0.075* | 0.555 (7) |
| C7B′ | −0.4663 (6) | 0.9414 (5) | 0.1581 (6) | 0.0317 (19) | 0.445 (7) |
| H7B1 | −0.4485 | 1.0055 | 0.1617 | 0.038* | 0.445 (7) |
| H7B2 | −0.5349 | 0.9392 | 0.1343 | 0.038* | 0.445 (7) |
| C8B′ | −0.4528 (5) | 0.9071 (6) | 0.2546 (6) | 0.043 (2) | 0.445 (7) |
| H8B1 | −0.4764 | 0.8455 | 0.2548 | 0.065* | 0.445 (7) |
| H8B2 | −0.4877 | 0.9455 | 0.2897 | 0.065* | 0.445 (7) |
| H8B3 | −0.3856 | 0.9082 | 0.2811 | 0.065* | 0.445 (7) |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| S1 | 0.0266 (4) | 0.0218 (4) | 0.0167 (3) | −0.0018 (3) | 0.0055 (3) | −0.0007 (3) |
| S2 | 0.0321 (4) | 0.0230 (4) | 0.0364 (4) | 0.0024 (3) | 0.0098 (3) | 0.0027 (3) |
| O1 | 0.0309 (11) | 0.0270 (11) | 0.0181 (10) | −0.0065 (9) | 0.0018 (8) | 0.0002 (9) |
| O2 | 0.0308 (11) | 0.0222 (11) | 0.0274 (11) | −0.0013 (9) | 0.0027 (9) | 0.0056 (9) |
| N2′ | 0.0287 (13) | 0.0192 (12) | 0.0243 (13) | −0.0049 (10) | 0.0079 (10) | −0.0017 (10) |
| N1 | 0.0256 (12) | 0.0169 (12) | 0.0169 (12) | −0.0017 (9) | 0.0071 (9) | −0.0031 (10) |
| N2 | 0.0316 (13) | 0.0152 (11) | 0.0168 (12) | 0.0004 (10) | 0.0050 (10) | 0.0010 (10) |
| C2 | 0.0179 (13) | 0.0200 (14) | 0.0204 (14) | 0.0008 (11) | 0.0070 (11) | −0.0023 (12) |
| C5 | 0.0225 (14) | 0.0189 (14) | 0.0184 (14) | −0.0010 (11) | 0.0063 (11) | −0.0029 (12) |
| N1′ | 0.0250 (13) | 0.0228 (13) | 0.0239 (13) | −0.0058 (10) | 0.0074 (10) | −0.0033 (10) |
| C4 | 0.0276 (15) | 0.0203 (14) | 0.0209 (14) | −0.0030 (12) | 0.0084 (12) | −0.0030 (12) |
| C6 | 0.0274 (15) | 0.0158 (13) | 0.0161 (14) | 0.0006 (11) | 0.0049 (11) | 0.0004 (11) |
| C6′ | 0.0288 (15) | 0.0207 (14) | 0.0259 (15) | −0.0053 (12) | 0.0119 (12) | −0.0054 (13) |
| C14′ | 0.0159 (14) | 0.0205 (14) | 0.0316 (16) | 0.0027 (11) | 0.0063 (12) | 0.0011 (12) |
| C1′ | 0.0311 (16) | 0.0266 (16) | 0.0307 (17) | −0.0075 (13) | 0.0077 (13) | 0.0010 (13) |
| C3 | 0.0219 (14) | 0.0221 (15) | 0.0214 (15) | 0.0016 (11) | 0.0072 (11) | −0.0015 (12) |
| C10′ | 0.0396 (18) | 0.0244 (15) | 0.0285 (17) | −0.0106 (13) | 0.0181 (14) | −0.0056 (14) |
| O1′ | 0.0527 (17) | 0.0398 (15) | 0.140 (3) | −0.0169 (13) | 0.0657 (19) | −0.0429 (17) |
| C5′ | 0.0310 (16) | 0.0253 (16) | 0.0264 (16) | −0.0050 (12) | 0.0128 (13) | −0.0003 (13) |
| C11 | 0.0276 (16) | 0.0446 (19) | 0.0212 (15) | 0.0020 (14) | 0.0040 (12) | −0.0039 (14) |
| C9′ | 0.0226 (15) | 0.0207 (14) | 0.0295 (16) | 0.0010 (11) | 0.0129 (12) | −0.0039 (12) |
| C9 | 0.0282 (15) | 0.0249 (15) | 0.0138 (14) | −0.0062 (12) | 0.0034 (11) | −0.0012 (12) |
| C10 | 0.0273 (16) | 0.0288 (16) | 0.0180 (14) | −0.0021 (12) | 0.0046 (12) | −0.0005 (12) |
| C16′ | 0.0282 (16) | 0.0177 (14) | 0.0386 (18) | −0.0026 (12) | 0.0030 (13) | 0.0005 (13) |
| C2′ | 0.0316 (16) | 0.0238 (15) | 0.0162 (14) | −0.0030 (12) | 0.0052 (12) | 0.0039 (12) |
| C4′ | 0.0300 (16) | 0.0274 (16) | 0.0171 (14) | −0.0040 (12) | 0.0077 (12) | 0.0031 (12) |
| C7 | 0.0302 (16) | 0.0400 (18) | 0.0194 (15) | −0.0028 (14) | 0.0021 (12) | 0.0006 (14) |
| C1 | 0.050 (2) | 0.0220 (15) | 0.0257 (16) | −0.0104 (14) | 0.0039 (14) | −0.0001 (13) |
| C16 | 0.050 (2) | 0.0264 (16) | 0.0251 (16) | −0.0083 (14) | 0.0100 (14) | 0.0013 (13) |
| C12′ | 0.0326 (17) | 0.0257 (16) | 0.0315 (17) | 0.0061 (13) | 0.0133 (13) | 0.0064 (14) |
| C14 | 0.0345 (17) | 0.0302 (16) | 0.0166 (14) | −0.0075 (13) | 0.0042 (12) | 0.0007 (13) |
| C13 | 0.0389 (19) | 0.0416 (19) | 0.0249 (16) | −0.0154 (15) | 0.0084 (14) | 0.0032 (15) |
| O2′ | 0.0587 (18) | 0.0531 (17) | 0.139 (3) | −0.0233 (14) | 0.069 (2) | −0.0380 (19) |
| C11′ | 0.0317 (17) | 0.0310 (17) | 0.0316 (17) | −0.0010 (13) | 0.0136 (13) | −0.0023 (14) |
| C13′ | 0.0251 (16) | 0.0206 (15) | 0.0420 (19) | 0.0016 (12) | 0.0085 (13) | 0.0033 (14) |
| C8 | 0.058 (2) | 0.052 (2) | 0.0238 (17) | −0.0221 (18) | 0.0064 (16) | −0.0058 (16) |
| C15′ | 0.055 (2) | 0.049 (2) | 0.0278 (18) | −0.0102 (17) | 0.0109 (16) | −0.0017 (16) |
| C15 | 0.0326 (18) | 0.060 (2) | 0.0347 (19) | 0.0101 (16) | 0.0073 (14) | −0.0096 (17) |
| C12 | 0.0258 (17) | 0.058 (2) | 0.0282 (17) | −0.0070 (15) | 0.0093 (13) | −0.0019 (16) |
| C3′ | 0.046 (2) | 0.038 (2) | 0.077 (3) | −0.0149 (17) | 0.039 (2) | −0.0178 (19) |
| C7A′ | 0.042 (4) | 0.052 (5) | 0.091 (7) | 0.007 (4) | 0.033 (5) | −0.015 (5) |
| C8A′ | 0.035 (4) | 0.037 (4) | 0.080 (5) | 0.009 (3) | 0.015 (3) | −0.023 (4) |
| C7B′ | 0.030 (4) | 0.022 (4) | 0.047 (5) | 0.005 (3) | 0.016 (4) | −0.008 (4) |
| C8B′ | 0.032 (4) | 0.050 (5) | 0.051 (5) | −0.005 (4) | 0.012 (4) | −0.011 (4) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| S1—C2 | 1.698 (3) | C10—H10 | 0.9500 |
| S2—C2′ | 1.687 (3) | C16′—H2′1 | 0.9800 |
| O1—C3 | 1.331 (3) | C16′—H2′2 | 0.9800 |
| O1—C7 | 1.459 (3) | C16′—H2′3 | 0.9800 |
| O2—C3 | 1.217 (3) | C7—C8 | 1.489 (4) |
| N2′—C2′ | 1.361 (4) | C7—H7A | 0.9900 |
| N2′—C4′ | 1.389 (4) | C7—H7B | 0.9900 |
| N2′—H2′ | 0.8800 | C1—H1A | 0.9800 |
| N1—C2 | 1.310 (3) | C1—H1B | 0.9800 |
| N1—C6 | 1.460 (3) | C1—H1C | 0.9800 |
| N1—H1 | 0.8800 | C16—C14 | 1.501 (4) |
| N2—C2 | 1.360 (3) | C16—H16A | 0.9800 |
| N2—C4 | 1.398 (3) | C16—H16B | 0.9800 |
| N2—H2 | 0.8800 | C16—H16C | 0.9800 |
| C5—C4 | 1.343 (4) | C12′—C13′ | 1.382 (4) |
| C5—C3 | 1.467 (4) | C12′—C11′ | 1.383 (4) |
| C5—C6 | 1.513 (4) | C12′—H12′ | 0.9500 |
| N1′—C2′ | 1.328 (4) | C14—C13 | 1.403 (4) |
| N1′—C6′ | 1.477 (4) | C13—C12 | 1.381 (5) |
| N1′—H1′ | 0.8800 | C13—H13 | 0.9500 |
| C4—C1 | 1.499 (4) | O2′—C3′ | 1.208 (4) |
| C6—C9 | 1.529 (4) | C11′—C15′ | 1.512 (5) |
| C6—H6 | 1.0000 | C13′—H13′ | 0.9500 |
| C6′—C5′ | 1.511 (4) | C8—H8A | 0.9800 |
| C6′—C9′ | 1.533 (4) | C8—H8B | 0.9800 |
| C6′—H6′ | 1.0000 | C8—H8C | 0.9800 |
| C14′—C13′ | 1.391 (4) | C15′—H3′1 | 0.9800 |
| C14′—C9′ | 1.405 (4) | C15′—H3′2 | 0.9800 |
| C14′—C16′ | 1.503 (4) | C15′—H3′3 | 0.9800 |
| C1′—C4′ | 1.492 (4) | C15—H15A | 0.9800 |
| C1′—H1′1 | 0.9800 | C15—H15B | 0.9800 |
| C1′—H1′2 | 0.9800 | C15—H15C | 0.9800 |
| C1′—H1′3 | 0.9800 | C12—H12 | 0.9500 |
| C10′—C11′ | 1.388 (4) | C7A′—C8A′ | 1.479 (10) |
| C10′—C9′ | 1.389 (4) | C7A′—H7A1 | 0.9900 |
| C10′—H10′ | 0.9500 | C7A′—H7A2 | 0.9900 |
| O1′—C3′ | 1.344 (4) | C8A′—H8A1 | 0.9800 |
| O1′—C7B′ | 1.527 (7) | C8A′—H8A2 | 0.9800 |
| O1′—C7A′ | 1.536 (7) | C8A′—H8A3 | 0.9800 |
| C5′—C4′ | 1.351 (4) | C7B′—C8B′ | 1.527 (12) |
| C5′—C3′ | 1.459 (4) | C7B′—H7B1 | 0.9900 |
| C11—C12 | 1.383 (5) | C7B′—H7B2 | 0.9900 |
| C11—C10 | 1.397 (4) | C8B′—H8B1 | 0.9800 |
| C11—C15 | 1.508 (5) | C8B′—H8B2 | 0.9800 |
| C9—C10 | 1.395 (4) | C8B′—H8B3 | 0.9800 |
| C9—C14 | 1.404 (4) | | |

| | | | |
|---|---|---|---|
| C3—O1—C7 | 115.5 (2) | C8—C7—H7A | 110.4 |
| C2′—N2′—C4′ | 124.5 (2) | O1—C7—H7B | 110.4 |
| C2′—N2′—H2′ | 117.8 | C8—C7—H7B | 110.4 |
| C4′—N2′—H2′ | 117.8 | H7A—C7—H7B | 108.6 |
| C2—N1—C6 | 125.8 (2) | C4—C1—H1A | 109.5 |
| C2—N1—H1 | 117.1 | C4—C1—H1B | 109.5 |
| C6—N1—H1 | 117.1 | H1A—C1—H1B | 109.5 |
| C2—N2—C4 | 122.8 (2) | C4—C1—H1C | 109.5 |
| C2—N2—H2 | 118.6 | H1A—C1—H1C | 109.5 |
| C4—N2—H2 | 118.6 | H1B—C1—H1C | 109.5 |
| N1—C2—N2 | 117.1 (2) | C14—C16—H16A | 109.5 |
| N1—C2—S1 | 122.8 (2) | C14—C16—H16B | 109.5 |
| N2—C2—S1 | 120.1 (2) | H16A—C16—H16B | 109.5 |
| C4—C5—C3 | 126.5 (3) | C14—C16—H16C | 109.5 |
| C4—C5—C6 | 120.9 (2) | H16A—C16—H16C | 109.5 |
| C3—C5—C6 | 112.6 (2) | H16B—C16—H16C | 109.5 |
| C2′—N1′—C6′ | 125.1 (2) | C13′—C12′—C11′ | 120.6 (3) |
| C2′—N1′—H1′ | 117.4 | C13′—C12′—H12′ | 119.7 |
| C6′—N1′—H1′ | 117.4 | C11′—C12′—H12′ | 119.7 |
| C5—C4—N2 | 118.7 (2) | C13—C14—C9 | 117.4 (3) |
| C5—C4—C1 | 127.4 (3) | C13—C14—C16 | 119.9 (3) |
| N2—C4—C1 | 113.9 (2) | C9—C14—C16 | 122.7 (3) |
| N1—C6—C5 | 109.1 (2) | C12—C13—C14 | 122.0 (3) |
| N1—C6—C9 | 110.1 (2) | C12—C13—H13 | 119.0 |
| C5—C6—C9 | 112.7 (2) | C14—C13—H13 | 119.0 |
| N1—C6—H6 | 108.2 | C12′—C11′—C10′ | 117.7 (3) |
| C5—C6—H6 | 108.2 | C12′—C11′—C15′ | 120.9 (3) |
| C9—C6—H6 | 108.2 | C10′—C11′—C15′ | 121.4 (3) |
| N1′—C6′—C5′ | 108.9 (2) | C12′—C13′—C14′ | 122.3 (3) |
| N1′—C6′—C9′ | 109.8 (2) | C12′—C13′—H13′ | 118.8 |
| C5′—C6′—C9′ | 113.9 (2) | C14′—C13′—H13′ | 118.8 |
| N1′—C6′—H6′ | 108.0 | C7—C8—H8A | 109.5 |
| C5′—C6′—H6′ | 108.0 | C7—C8—H8B | 109.5 |
| C9′—C6′—H6′ | 108.0 | H8A—C8—H8B | 109.5 |
| C13′—C14′—C9′ | 117.3 (3) | C7—C8—H8C | 109.5 |
| C13′—C14′—C16′ | 120.5 (3) | H8A—C8—H8C | 109.5 |
| C9′—C14′—C16′ | 122.2 (3) | H8B—C8—H8C | 109.5 |
| C4′—C1′—H1′1 | 109.5 | C11′—C15′—H3′1 | 109.5 |
| C4′—C1′—H1′2 | 109.5 | C11′—C15′—H3′2 | 109.5 |
| H1′1—C1′—H1′2 | 109.5 | H3′1—C15′—H3′2 | 109.5 |
| C4′—C1′—H1′3 | 109.5 | C11′—C15′—H3′3 | 109.5 |
| H1′1—C1′—H1′3 | 109.5 | H3′1—C15′—H3′3 | 109.5 |
| H1′2—C1′—H1′3 | 109.5 | H3′2—C15′—H3′3 | 109.5 |
| O2—C3—O1 | 123.2 (3) | C11—C15—H15A | 109.5 |
| O2—C3—C5 | 121.2 (3) | C11—C15—H15B | 109.5 |
| O1—C3—C5 | 115.6 (2) | H15A—C15—H15B | 109.5 |
| C11′—C10′—C9′ | 122.3 (3) | C11—C15—H15C | 109.5 |

| | | | |
|---|---|---|---|
| C11′—C10′—H10′ | 118.8 | H15A—C15—H15C | 109.5 |
| C9′—C10′—H10′ | 118.8 | H15B—C15—H15C | 109.5 |
| C3′—O1′—C7B′ | 113.4 (4) | C13—C12—C11 | 121.1 (3) |
| C3′—O1′—C7A′ | 116.2 (4) | C13—C12—H12 | 119.5 |
| C4′—C5′—C3′ | 122.0 (3) | C11—C12—H12 | 119.5 |
| C4′—C5′—C6′ | 120.3 (3) | O2′—C3′—O1′ | 122.2 (3) |
| C3′—C5′—C6′ | 117.7 (3) | O2′—C3′—C5′ | 127.3 (3) |
| C12—C11—C10 | 117.4 (3) | O1′—C3′—C5′ | 110.5 (3) |
| C12—C11—C15 | 121.9 (3) | C8A′—C7A′—O1′ | 105.4 (5) |
| C10—C11—C15 | 120.7 (3) | C8A′—C7A′—H7A1 | 110.7 |
| C10′—C9′—C14′ | 119.7 (3) | O1′—C7A′—H7A1 | 110.7 |
| C10′—C9′—C6′ | 119.4 (2) | C8A′—C7A′—H7A2 | 110.7 |
| C14′—C9′—C6′ | 120.9 (3) | O1′—C7A′—H7A2 | 110.7 |
| C10—C9—C14 | 119.7 (3) | H7A1—C7A′—H7A2 | 108.8 |
| C10—C9—C6 | 118.3 (2) | C7A′—C8A′—H8A1 | 109.5 |
| C14—C9—C6 | 122.0 (3) | C7A′—C8A′—H8A2 | 109.5 |
| C9—C10—C11 | 122.4 (3) | H8A1—C8A′—H8A2 | 109.5 |
| C9—C10—H10 | 118.8 | C7A′—C8A′—H8A3 | 109.5 |
| C11—C10—H10 | 118.8 | H8A1—C8A′—H8A3 | 109.5 |
| C14′—C16′—H2′1 | 109.5 | H8A2—C8A′—H8A3 | 109.5 |
| C14′—C16′—H2′2 | 109.5 | C8B′—C7B′—O1′ | 123.0 (6) |
| H2′1—C16′—H2′2 | 109.5 | C8B′—C7B′—H7B1 | 106.6 |
| C14′—C16′—H2′3 | 109.5 | O1′—C7B′—H7B1 | 106.6 |
| H2′1—C16′—H2′3 | 109.5 | C8B′—C7B′—H7B2 | 106.6 |
| H2′2—C16′—H2′3 | 109.5 | O1′—C7B′—H7B2 | 106.6 |
| N1′—C2′—N2′ | 115.6 (3) | H7B1—C7B′—H7B2 | 106.5 |
| N1′—C2′—S2 | 123.1 (2) | C7B′—C8B′—H8B1 | 109.5 |
| N2′—C2′—S2 | 121.4 (2) | C7B′—C8B′—H8B2 | 109.5 |
| C5′—C4′—N2′ | 118.8 (3) | H8B1—C8B′—H8B2 | 109.5 |
| C5′—C4′—C1′ | 127.5 (3) | C7B′—C8B′—H8B3 | 109.5 |
| N2′—C4′—C1′ | 113.7 (2) | H8B1—C8B′—H8B3 | 109.5 |
| O1—C7—C8 | 106.6 (3) | H8B2—C8B′—H8B3 | 109.5 |
| O1—C7—H7A | 110.4 | | |

| | | | |
|---|---|---|---|
| C6—N1—C2—N2 | −9.6 (4) | C14—C9—C10—C11 | −0.2 (4) |
| C6—N1—C2—S1 | 171.3 (2) | C6—C9—C10—C11 | −179.5 (3) |
| C4—N2—C2—N1 | −11.8 (4) | C12—C11—C10—C9 | −1.3 (4) |
| C4—N2—C2—S1 | 167.3 (2) | C15—C11—C10—C9 | 177.6 (3) |
| C3—C5—C4—N2 | −175.8 (2) | C6′—N1′—C2′—N2′ | −15.3 (4) |
| C6—C5—C4—N2 | 3.9 (4) | C6′—N1′—C2′—S2 | 166.0 (2) |
| C3—C5—C4—C1 | 3.6 (5) | C4′—N2′—C2′—N1′ | −8.7 (4) |
| C6—C5—C4—C1 | −176.7 (3) | C4′—N2′—C2′—S2 | 170.1 (2) |
| C2—N2—C4—C5 | 14.3 (4) | C3′—C5′—C4′—N2′ | −176.1 (3) |
| C2—N2—C4—C1 | −165.2 (3) | C6′—C5′—C4′—N2′ | 3.7 (4) |
| C2—N1—C6—C5 | 24.5 (3) | C3′—C5′—C4′—C1′ | 1.9 (5) |
| C2—N1—C6—C9 | −99.7 (3) | C6′—C5′—C4′—C1′ | −178.3 (3) |
| C4—C5—C6—N1 | −20.8 (3) | C2′—N2′—C4′—C5′ | 14.1 (4) |
| C3—C5—C6—N1 | 159.0 (2) | C2′—N2′—C4′—C1′ | −164.1 (3) |

| | | | |
|---|---|---|---|
| C4—C5—C6—C9 | 101.9 (3) | C3—O1—C7—C8 | 170.5 (3) |
| C3—C5—C6—C9 | −78.3 (3) | C10—C9—C14—C13 | 1.1 (4) |
| C2′—N1′—C6′—C5′ | 29.5 (4) | C6—C9—C14—C13 | −179.7 (3) |
| C2′—N1′—C6′—C9′ | −95.9 (3) | C10—C9—C14—C16 | −178.4 (3) |
| C7—O1—C3—O2 | 1.9 (4) | C6—C9—C14—C16 | 0.9 (4) |
| C7—O1—C3—C5 | −177.8 (2) | C9—C14—C13—C12 | −0.4 (4) |
| C4—C5—C3—O2 | −178.8 (3) | C16—C14—C13—C12 | 179.1 (3) |
| C6—C5—C3—O2 | 1.5 (4) | C13′—C12′—C11′—C10′ | −1.5 (4) |
| C4—C5—C3—O1 | 0.9 (4) | C13′—C12′—C11′—C15′ | 176.3 (3) |
| C6—C5—C3—O1 | −178.8 (2) | C9′—C10′—C11′—C12′ | 1.1 (4) |
| N1′—C6′—C5′—C4′ | −22.4 (4) | C9′—C10′—C11′—C15′ | −176.6 (3) |
| C9′—C6′—C5′—C4′ | 100.5 (3) | C11′—C12′—C13′—C14′ | −0.1 (4) |
| N1′—C6′—C5′—C3′ | 157.5 (3) | C9′—C14′—C13′—C12′ | 2.0 (4) |
| C9′—C6′—C5′—C3′ | −79.6 (4) | C16′—C14′—C13′—C12′ | −176.7 (3) |
| C11′—C10′—C9′—C14′ | 0.8 (4) | C14—C13—C12—C11 | −1.2 (5) |
| C11′—C10′—C9′—C6′ | −178.6 (3) | C10—C11—C12—C13 | 2.0 (5) |
| C13′—C14′—C9′—C10′ | −2.3 (4) | C15—C11—C12—C13 | −176.9 (3) |
| C16′—C14′—C9′—C10′ | 176.4 (3) | C7B′—O1′—C3′—O2′ | 25.2 (7) |
| C13′—C14′—C9′—C6′ | 177.1 (2) | C7A′—O1′—C3′—O2′ | −18.2 (8) |
| C16′—C14′—C9′—C6′ | −4.2 (4) | C7B′—O1′—C3′—C5′ | −154.5 (5) |
| N1′—C6′—C9′—C10′ | 78.3 (3) | C7A′—O1′—C3′—C5′ | 162.2 (5) |
| C5′—C6′—C9′—C10′ | −44.1 (3) | C4′—C5′—C3′—O2′ | −3.2 (7) |
| N1′—C6′—C9′—C14′ | −101.1 (3) | C6′—C5′—C3′—O2′ | 177.0 (4) |
| C5′—C6′—C9′—C14′ | 136.5 (3) | C4′—C5′—C3′—O1′ | 176.4 (3) |
| N1—C6—C9—C10 | 69.9 (3) | C6′—C5′—C3′—O1′ | −3.4 (5) |
| C5—C6—C9—C10 | −52.2 (3) | C3′—O1′—C7A′—C8A′ | −175.3 (6) |
| N1—C6—C9—C14 | −109.4 (3) | C3′—O1′—C7B′—C8B′ | 65.6 (8) |
| C5—C6—C9—C14 | 128.5 (3) | | |

*Hydrogen-bond geometry (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N1—H1···S1$^{i}$ | 0.88 | 2.47 | 3.315 (2) | 160 |
| N1′—H1′···S1 | 0.88 | 2.49 | 3.316 (2) | 156 |
| N2—H2···S2 | 0.88 | 2.65 | 3.431 (2) | 148 |
| N2′—H2′···O2$^{ii}$ | 0.88 | 1.97 | 2.833 (3) | 168 |
| C1—H1*C*···O2′$^{iii}$ | 0.98 | 2.58 | 3.477 (5) | 152 |
| C1′—H1′2···O2$^{ii}$ | 0.98 | 2.56 | 3.377 (4) | 141 |
| C16—H16*A*···S1$^{i}$ | 0.98 | 2.77 | 3.717 (3) | 162 |

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