Acta Crystallographica Section E
**Structure Reports Online**
ISSN 1600-5368

# 1,5-Dimethyl-4-{[(3-methyl-5-oxo-1-phenyl-4,5-dihydro-1*H*-pyrazol-4-yl-idene)(thiophen-2-yl)methyl]amino}-2-phenyl-1*H*-pyrazol-3(2*H*)-one

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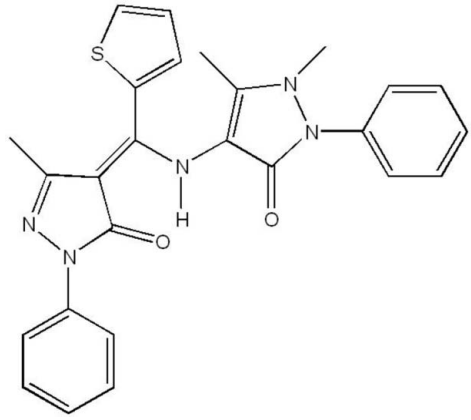
Received 10 January 2011; accepted 18 January 2011

Key indicators: single-crystal X-ray study; $T$ = 293 K; mean $\sigma$(C–C) = 0.003 Å; disorder in main residue; $R$ factor = 0.049; $wR$ factor = 0.144; data-to-parameter ratio = 17.3.

In the title compound, $C_{26}H_{23}N_5O_2S$, an intramolecular N—H···O interaction generates an $S$(6) ring. The essentially planar $S$(6) and pyrazole rings [maximum deviations = −0.0270 (14) and 0.0195 (15) Å, respectively] are nearly coplanar, making a dihedral angle of 3.94 (6)°. The $S$(6) ring makes dihedral angles of 23.79 (6), 78.53 (6) and 67.91 (6)° with the pyrazolone ring, the pyrazole ring and the benzene ring of antipyrine, respectively. The structure exhibits a thienyl-ring flip disorder with occupancy factors in the ratio 0.82:0.18.

## Related literature

For general background to pyrazolones, see: Casas *et al.* (2007). For the antibacterial activity of pyrazolone Schiff bases, see: Zhang *et al.* (2008); Li *et al.* (2000). For our previous work in this area, see: Zhu *et al.* (2010*a*,*b*). For related structures, see: Shi *et al.* (2005); Goh *et al.* (2009). For disordered thienyl rings, see: Crundwell *et al.* (2003).



## Experimental

### Crystal data

$C_{26}H_{23}N_5O_2S$
$M_r$ = 469.55
Monoclinic, $C2/c$
$a$ = 27.098 (3) Å
$b$ = 7.9045 (8) Å
$c$ = 22.308 (2) Å
$\beta$ = 99.011 (8)°
$V$ = 4719.4 (9) Å$^3$
$Z$ = 8
Mo $K\alpha$ radiation
$\mu$ = 0.17 mm$^{-1}$
$T$ = 293 K
0.42 × 0.36 × 0.34 mm

### Data collection

Rigaku Saturn diffractometer
Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2008)
$T_{min}$ = 0.932, $T_{max}$ = 0.944
22080 measured reflections
5570 independent reflections
3806 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.037

### Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.049
$wR(F^2)$ = 0.144
$S$ = 1.02
5570 reflections
322 parameters
22 restraints
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.23 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.25 e Å$^{-3}$

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| N3—H3···O2 | 0.86 | 1.96 | 2.6631 (18) | 138 |

Data collection: *CrystalClear* (Rigaku, 2008); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996) and *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

The authors are grateful for financial support from the Spark Program Foundation of Science and Technology Department of China (research Nos. 09ZHXHNC07900 and 2010 GA610009). The authors also thank the Technical Staff Serving Enterprise Action Committee of the Science and Technology Department of China for financial support (research No. 2009 GJ A10022).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: DN2653).

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# supporting information

*Acta Cryst.* (2011). E**67**, o476–o477 [doi:10.1107/S1600536811002467]

## 1,5-Dimethyl-4-{[(3-methyl-5-oxo-1-phenyl-4,5-dihydro-1*H*-pyrazol-4-ylidene)(thiophen-2-yl)methyl]amino}-2-phenyl-1*H*-pyrazol-3(2*H*)-one

**Hualing Zhu, Litong Ban, Pingping Zhang, Xinxin Zhao and Junjie Ren**

### S1. Comment

Pyrazolones form a very important class of heterocycles due to their properties and applications (Casas *et al.*, 2007). Schiff-bases derived from 1-phenyl-3-methyl-4-acyl-5-pyrazolone have found extensive application in coordination chemistry (Shi *et al.*, 2005)and in antibacterial activation (Zhang *et al.*, 2008; Li *et al.*, 2000). In continuation of our studies on pyrazolone schiff bases (Zhu *et al.*, 2010*a*,*b*), we herein report the crystal structure of the title pyrazole compound.

The molecular structure of the title compound is shown in Fig. 1. An intramolecular N—H···O interaction generates a six- membered ring, producing an S(6) ring (O2 N3 C12 C17 C18), which stablizing the enamine–keto form of the compound. The S(6) ring and pyrazole ring (N4 N5 C17 C18 C19) are essentially planar,with the maximum deviations of -0.0270 (14) and 0.0195 (15) Å, respectively, at atoms C12 and C17.The two rings are coplanar to one another, as indicated by the dihedral angle formed between them of 3.94 (6)°. The S(6) ring makes dihedral angles of 23.79 (6)°,78.53 (6)° and 67.91 (6)° with the benzene ring of pyrazolone, the pyrazole ring and benzene ring of antipyrine,respectively. The bond lengths and angles agree well with those closely related pyrazole structures (Goh *et al.*, 2009)

The structure exhibits a thienyl-ring flip disorder with the occupancy factors in the ratio 82/18.

### S2. Experimental

The title compound was synthesized by refluxing the mixture of 1-phenyl-3-methyl-4-(2-thenoyl)pyrazolone-5 (HPMTP) (15*m* mol) and 4-antipyrine (15*m* mol) in ethanol (100 ml) over a steam bath for about 4 h, then the solution was cooled down to room temperature. After seven days, pale yellow block was obtained and dried in air. The product was recrystallized from ethanol which afforded pale yellow and acerate crystals suitable for *X*–ray analysis.

### S3. Refinement

During refinement, the thienyl ring showed evidence of ring-flip disorder which is common for unsubstituted 2- and 3-thienyl rings (Crundwell *et al.*, 2003). After finding three of the flipped disordered atoms in the difference map, the rest of the ring was generated and modeled. The occupancy factors of the disordered thienyl ring were first refine restraining the sum of the occupancy factore to be equal to 1.0. Once stabilised, the occupancy factors were fixed and not refined anymore. The final model suggested that the thienyl ring disorder was in the ratio 82/18. The disordered model was refined using the tools available in SHELXL-97 (Sheldrick, 2008): SADI for restraining distances, FLAT for constraining the thienyl rings to be planar, EXYZ for linking atoms occupying the same site and EADP to correlate anisotropic thermal parameters for related disordered atoms.

All H atoms were geometrically positioned and treated as riding on their parent atoms, with C—H = 0.93 Å for the aromatic, 0.96 Å for the methyl and N-H= 0.86 Å with $U_{iso}$(H)= 1.2 $U_{eq}$(Caromatic, N) or, 1.5$U_{eq}$(Cmethyl).

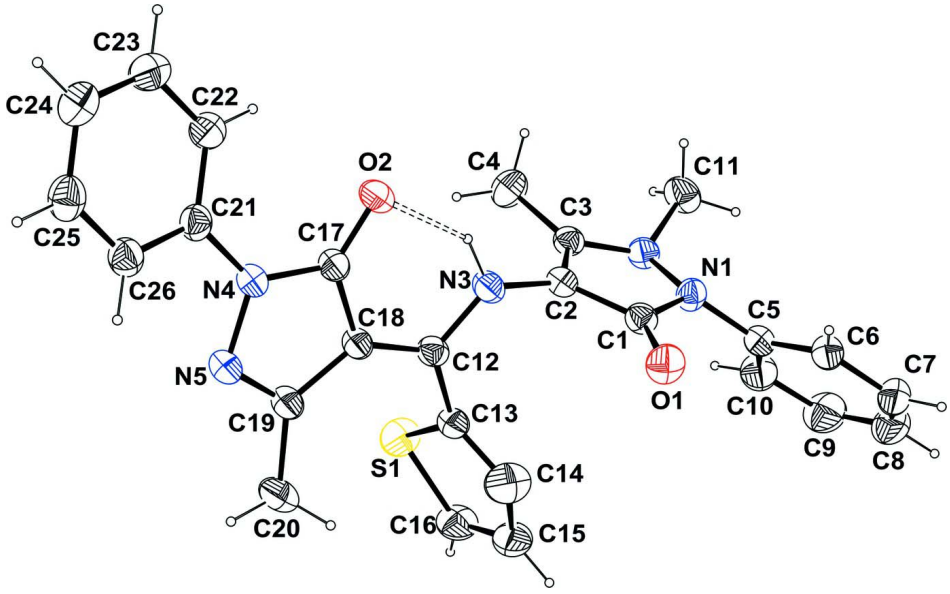


**Figure 1**

The molecular structure of the title compound with the atom numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. H atoms are presented as a small spheres of arbitrary radii. Only the major component of the disordered thienyl ring is represented for the sake of clarity.

**1,5-Dimethyl-4-{[(3-methyl-5-oxo-1-phenyl-4,5-dihydro-1*H*-pyrazol-4- ylidene)(thiophen-2-yl)methyl]amino}-2-phenyl-1*H*-pyrazol- 3(2*H*)-one**

*Crystal data*

$C_{26}H_{23}N_5O_2S$
$M_r$ = 469.55
Monoclinic, *C*2/*c*
Hall symbol: -C 2yc
*a* = 27.098 (3) Å
*b* = 7.9045 (8) Å
*c* = 22.308 (2) Å
*β* = 99.011 (8)°
*V* = 4719.4 (9) Å$^3$
*Z* = 8
*F*(000) = 1968
$D_x$ = 1.322 Mg m$^{-3}$
Mo *Kα* radiation, *λ* = 0.71075 Å
Cell parameters from 5913 reflections
*θ* = 2.6–27.9°
*μ* = 0.17 mm$^{-1}$
*T* = 293 K
Prism, colourless
0.42 × 0.36 × 0.34 mm

*Data collection*

Rigaku Saturn diffractometer
Radiation source: rotating anode
Multilayer monochromator
Detector resolution: 7.31 pixels mm$^{-1}$
*ω* scans
Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2008)
$T_{min}$ = 0.932, $T_{max}$ = 0.944
22080 measured reflections
5570 independent reflections
3806 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.037
$\theta_{max}$ = 27.9°, $\theta_{min}$ = 2.6°
*h* = −35→35
*k* = −10→8
*l* = −29→29

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.049$
$wR(F^2) = 0.144$
$S = 1.02$
5570 reflections
322 parameters
22 restraints
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
$w = 1/[\sigma^2(F_o^2) + (0.0825P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.003$
$\Delta\rho_{max} = 0.23$ e Å$^{-3}$
$\Delta\rho_{min} = -0.25$ 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.

**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 (Å²)*

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ | Occ. (<1) |
|---|---|---|---|---|---|
| O1 | 0.25433 (4) | 1.02510 (13) | 0.08661 (6) | 0.0607 (3) | |
| O2 | 0.08792 (4) | 0.72515 (16) | −0.01432 (5) | 0.0574 (3) | |
| N1 | 0.30507 (4) | 0.78662 (15) | 0.09168 (6) | 0.0454 (3) | |
| N2 | 0.29718 (5) | 0.61104 (15) | 0.09307 (6) | 0.0453 (3) | |
| N3 | 0.17055 (5) | 0.75910 (17) | 0.06681 (6) | 0.0490 (3) | |
| H3 | 0.1558 | 0.7573 | 0.0298 | 0.059* | |
| N4 | 0.01707 (5) | 0.77052 (16) | 0.03130 (6) | 0.0483 (3) | |
| N5 | 0.00673 (5) | 0.81903 (18) | 0.08851 (7) | 0.0531 (4) | |
| C1 | 0.25902 (6) | 0.87031 (19) | 0.08467 (7) | 0.0440 (4) | |
| C2 | 0.22290 (5) | 0.73667 (18) | 0.07704 (7) | 0.0418 (3) | |
| C3 | 0.24689 (6) | 0.58580 (18) | 0.07935 (7) | 0.0431 (3) | |
| C4 | 0.22546 (7) | 0.4148 (2) | 0.06696 (9) | 0.0652 (5) | |
| H4A | 0.1900 | 0.4190 | 0.0665 | 0.098* | |
| H4B | 0.2402 | 0.3383 | 0.0981 | 0.098* | |
| H4C | 0.2323 | 0.3762 | 0.0283 | 0.098* | |
| C5 | 0.35010 (6) | 0.8549 (2) | 0.12487 (7) | 0.0473 (4) | |
| C6 | 0.36892 (6) | 1.0029 (2) | 0.10435 (8) | 0.0560 (4) | |
| H6 | 0.3523 | 1.0563 | 0.0698 | 0.067* | |
| C7 | 0.41249 (7) | 1.0712 (3) | 0.13541 (11) | 0.0717 (6) | |
| H7 | 0.4250 | 1.1720 | 0.1223 | 0.086* | |
| C8 | 0.43721 (8) | 0.9902 (3) | 0.18544 (12) | 0.0836 (7) | |
| H8 | 0.4667 | 1.0357 | 0.2060 | 0.100* | |
| C9 | 0.41887 (8) | 0.8425 (3) | 0.20554 (10) | 0.0843 (6) | |
| H9 | 0.4363 | 0.7876 | 0.2392 | 0.101* | |
| C10 | 0.37464 (7) | 0.7747 (3) | 0.17596 (9) | 0.0655 (5) | |

| | | | | | |
|---|---|---|---|---|---|
| H10 | 0.3616 | 0.6765 | 0.1903 | 0.079* | |
| C11 | 0.33387 (7) | 0.4992 (2) | 0.07232 (9) | 0.0628 (5) | |
| H11A | 0.3337 | 0.3918 | 0.0924 | 0.094* | |
| H11B | 0.3665 | 0.5489 | 0.0816 | 0.094* | |
| H11C | 0.3256 | 0.4832 | 0.0293 | 0.094* | |
| C12 | 0.14164 (6) | 0.78314 (18) | 0.11001 (7) | 0.0431 (4) | |
| S1 | 0.16071 (3) | 0.63681 (8) | 0.22363 (3) | 0.0702 (2) | 0.82 |
| C13 | 0.16636 (6) | 0.79831 (19) | 0.17339 (7) | 0.0468 (4) | 0.82 |
| C14 | 0.19533 (11) | 0.9188 (3) | 0.20297 (12) | 0.0704 (8) | 0.82 |
| H14 | 0.2031 | 1.0169 | 0.1834 | 0.085* | 0.82 |
| C15 | 0.21288 (18) | 0.8917 (6) | 0.26270 (14) | 0.0765 (8) | 0.82 |
| H15 | 0.2330 | 0.9675 | 0.2874 | 0.092* | 0.82 |
| C16 | 0.19767 (14) | 0.7430 (5) | 0.28143 (13) | 0.0709 (9) | 0.82 |
| H16 | 0.2060 | 0.7018 | 0.3208 | 0.085* | 0.82 |
| S1′ | 0.20046 (19) | 0.9710 (5) | 0.1965 (2) | 0.0702 (2) | 0.18 |
| C13′ | 0.16636 (6) | 0.79831 (19) | 0.17339 (7) | 0.0468 (4) | 0.18 |
| C14′ | 0.1637 (5) | 0.6894 (16) | 0.2181 (5) | 0.0704 (8) | 0.18 |
| H14′ | 0.1463 | 0.5877 | 0.2123 | 0.085* | 0.18 |
| C15′ | 0.1879 (8) | 0.738 (2) | 0.2721 (6) | 0.0765 (8) | 0.18 |
| H15′ | 0.1895 | 0.6745 | 0.3075 | 0.092* | 0.18 |
| C16′ | 0.2097 (7) | 0.889 (2) | 0.2692 (6) | 0.0709 (9) | 0.18 |
| H16′ | 0.2278 | 0.9432 | 0.3025 | 0.085* | 0.18 |
| C17 | 0.06744 (5) | 0.75638 (19) | 0.03103 (7) | 0.0449 (4) | |
| C18 | 0.09039 (6) | 0.78841 (18) | 0.09237 (7) | 0.0437 (4) | |
| C19 | 0.04936 (6) | 0.8289 (2) | 0.12425 (8) | 0.0504 (4) | |
| C20 | 0.05032 (7) | 0.8851 (3) | 0.18855 (9) | 0.0727 (6) | |
| H20A | 0.0181 | 0.9285 | 0.1934 | 0.109* | |
| H20B | 0.0750 | 0.9721 | 0.1982 | 0.109* | |
| H20C | 0.0585 | 0.7907 | 0.2153 | 0.109* | |
| C21 | −0.02273 (6) | 0.75001 (19) | −0.01723 (7) | 0.0468 (4) | |
| C22 | −0.01595 (7) | 0.6573 (2) | −0.06807 (8) | 0.0579 (4) | |
| H22 | 0.0149 | 0.6082 | −0.0706 | 0.069* | |
| C23 | −0.05544 (7) | 0.6384 (2) | −0.11491 (9) | 0.0648 (5) | |
| H23 | −0.0511 | 0.5759 | −0.1490 | 0.078* | |
| C24 | −0.10124 (7) | 0.7112 (2) | −0.11174 (9) | 0.0650 (5) | |
| H24 | −0.1276 | 0.6986 | −0.1436 | 0.078* | |
| C25 | −0.10744 (7) | 0.8021 (2) | −0.06118 (9) | 0.0618 (5) | |
| H25 | −0.1383 | 0.8510 | −0.0588 | 0.074* | |
| C26 | −0.06879 (6) | 0.8225 (2) | −0.01381 (9) | 0.0540 (4) | |
| H26 | −0.0735 | 0.8844 | 0.0203 | 0.065* | |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| O1 | 0.0648 (7) | 0.0375 (6) | 0.0805 (9) | 0.0072 (5) | 0.0132 (6) | 0.0016 (5) |
| O2 | 0.0493 (6) | 0.0790 (8) | 0.0465 (7) | 0.0004 (6) | 0.0160 (5) | −0.0109 (6) |
| N1 | 0.0438 (7) | 0.0364 (7) | 0.0564 (8) | 0.0001 (5) | 0.0095 (6) | −0.0004 (5) |
| N2 | 0.0477 (8) | 0.0353 (7) | 0.0541 (8) | 0.0042 (5) | 0.0122 (6) | −0.0015 (5) |

| | | | | | | |
|---|---|---|---|---|---|---|
| N3 | 0.0451 (7) | 0.0643 (8) | 0.0390 (7) | 0.0024 (6) | 0.0108 (6) | −0.0003 (6) |
| N4 | 0.0422 (7) | 0.0559 (8) | 0.0494 (8) | −0.0021 (6) | 0.0152 (6) | −0.0073 (6) |
| N5 | 0.0494 (8) | 0.0609 (9) | 0.0531 (8) | −0.0029 (6) | 0.0206 (7) | −0.0073 (6) |
| C1 | 0.0466 (9) | 0.0403 (8) | 0.0462 (9) | 0.0041 (7) | 0.0108 (7) | 0.0004 (6) |
| C2 | 0.0427 (8) | 0.0444 (8) | 0.0395 (8) | 0.0028 (6) | 0.0100 (6) | 0.0004 (6) |
| C3 | 0.0506 (9) | 0.0411 (8) | 0.0393 (8) | −0.0014 (7) | 0.0122 (7) | 0.0008 (6) |
| C4 | 0.0727 (12) | 0.0466 (10) | 0.0756 (13) | −0.0091 (9) | 0.0088 (10) | −0.0026 (8) |
| C5 | 0.0449 (9) | 0.0492 (9) | 0.0496 (9) | −0.0004 (7) | 0.0132 (7) | −0.0053 (7) |
| C6 | 0.0548 (10) | 0.0545 (10) | 0.0615 (11) | −0.0064 (8) | 0.0180 (8) | −0.0054 (8) |
| C7 | 0.0580 (12) | 0.0731 (13) | 0.0879 (15) | −0.0165 (10) | 0.0234 (11) | −0.0217 (11) |
| C8 | 0.0542 (12) | 0.1040 (18) | 0.0905 (17) | −0.0113 (12) | 0.0047 (12) | −0.0319 (14) |
| C9 | 0.0697 (14) | 0.1072 (18) | 0.0688 (14) | 0.0025 (13) | −0.0116 (11) | −0.0062 (13) |
| C10 | 0.0655 (12) | 0.0736 (13) | 0.0562 (11) | −0.0005 (10) | 0.0059 (9) | 0.0044 (9) |
| C11 | 0.0650 (11) | 0.0491 (10) | 0.0797 (13) | 0.0140 (8) | 0.0277 (10) | −0.0015 (9) |
| C12 | 0.0502 (9) | 0.0384 (8) | 0.0426 (8) | −0.0014 (6) | 0.0134 (7) | 0.0004 (6) |
| S1 | 0.0933 (5) | 0.0628 (5) | 0.0532 (4) | −0.0107 (4) | 0.0077 (3) | 0.0143 (3) |
| C13 | 0.0493 (9) | 0.0510 (9) | 0.0418 (8) | 0.0006 (7) | 0.0129 (7) | −0.0007 (7) |
| C14 | 0.111 (2) | 0.0564 (18) | 0.0461 (14) | −0.0152 (16) | 0.0183 (13) | 0.0058 (12) |
| C15 | 0.0871 (19) | 0.096 (2) | 0.0469 (15) | −0.0203 (15) | 0.0134 (14) | −0.0138 (14) |
| C16 | 0.079 (2) | 0.093 (2) | 0.0389 (14) | 0.0077 (16) | 0.0025 (13) | 0.0086 (14) |
| S1′ | 0.0933 (5) | 0.0628 (5) | 0.0532 (4) | −0.0107 (4) | 0.0077 (3) | 0.0143 (3) |
| C13′ | 0.0493 (9) | 0.0510 (9) | 0.0418 (8) | 0.0006 (7) | 0.0129 (7) | −0.0007 (7) |
| C14′ | 0.111 (2) | 0.0564 (18) | 0.0461 (14) | −0.0152 (16) | 0.0183 (13) | 0.0058 (12) |
| C15′ | 0.0871 (19) | 0.096 (2) | 0.0469 (15) | −0.0203 (15) | 0.0134 (14) | −0.0138 (14) |
| C16′ | 0.079 (2) | 0.093 (2) | 0.0389 (14) | 0.0077 (16) | 0.0025 (13) | 0.0086 (14) |
| C17 | 0.0441 (9) | 0.0447 (8) | 0.0481 (9) | −0.0024 (7) | 0.0144 (7) | −0.0034 (6) |
| C18 | 0.0440 (9) | 0.0450 (8) | 0.0447 (8) | −0.0030 (6) | 0.0149 (7) | −0.0023 (6) |
| C19 | 0.0507 (10) | 0.0533 (9) | 0.0509 (9) | −0.0034 (7) | 0.0197 (8) | −0.0041 (7) |
| C20 | 0.0693 (12) | 0.0975 (16) | 0.0566 (11) | 0.0001 (10) | 0.0262 (9) | −0.0158 (10) |
| C21 | 0.0442 (9) | 0.0437 (8) | 0.0537 (9) | −0.0050 (7) | 0.0113 (7) | 0.0004 (7) |
| C22 | 0.0509 (10) | 0.0610 (11) | 0.0621 (11) | 0.0011 (8) | 0.0097 (8) | −0.0105 (8) |
| C23 | 0.0668 (12) | 0.0650 (12) | 0.0613 (12) | −0.0039 (9) | 0.0056 (9) | −0.0120 (9) |
| C24 | 0.0592 (11) | 0.0631 (12) | 0.0688 (12) | −0.0045 (9) | −0.0019 (9) | 0.0008 (9) |
| C25 | 0.0492 (10) | 0.0544 (11) | 0.0810 (14) | 0.0022 (8) | 0.0077 (9) | 0.0043 (9) |
| C26 | 0.0488 (10) | 0.0487 (9) | 0.0660 (11) | −0.0009 (7) | 0.0138 (8) | −0.0033 (8) |

*Geometric parameters (Å, º)*

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| O1—C1 | 1.2316 (17) | C12—C18 | 1.384 (2) |
| O2—C17 | 1.2524 (16) | C12—C13 | 1.472 (2) |
| N1—C1 | 1.3994 (19) | S1—C13 | 1.7213 (16) |
| N1—N2 | 1.4054 (17) | S1—C16 | 1.722 (3) |
| N1—C5 | 1.430 (2) | C13—C14 | 1.340 (3) |
| N2—C3 | 1.3637 (19) | C14—C15 | 1.360 (4) |
| N2—C11 | 1.4590 (19) | C14—H14 | 0.9300 |
| N3—C12 | 1.3471 (18) | C15—C16 | 1.335 (3) |
| N3—C2 | 1.412 (2) | C15—H15 | 0.9300 |
| N3—H3 | 0.8600 | C16—H16 | 0.9300 |

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|---|---|---|---|
| N4—C17 | 1.3703 (19) | S1′—C16′ | 1.728 (10) |
| N4—N5 | 1.4023 (17) | C14′—C15′ | 1.336 (8) |
| N4—C21 | 1.413 (2) | C14′—H14′ | 0.9300 |
| N5—C19 | 1.299 (2) | C15′—C16′ | 1.336 (8) |
| C1—C2 | 1.432 (2) | C15′—H15′ | 0.9300 |
| C2—C3 | 1.355 (2) | C16′—H16′ | 0.9300 |
| C3—C4 | 1.480 (2) | C17—C18 | 1.434 (2) |
| C4—H4A | 0.9600 | C18—C19 | 1.446 (2) |
| C4—H4B | 0.9600 | C19—C20 | 1.498 (2) |
| C4—H4C | 0.9600 | C20—H20A | 0.9600 |
| C5—C10 | 1.380 (2) | C20—H20B | 0.9600 |
| C5—C6 | 1.383 (2) | C20—H20C | 0.9600 |
| C6—C7 | 1.382 (3) | C21—C26 | 1.386 (2) |
| C6—H6 | 0.9300 | C21—C22 | 1.387 (2) |
| C7—C8 | 1.368 (3) | C22—C23 | 1.382 (3) |
| C7—H7 | 0.9300 | C22—H22 | 0.9300 |
| C8—C9 | 1.371 (3) | C23—C24 | 1.380 (3) |
| C8—H8 | 0.9300 | C23—H23 | 0.9300 |
| C9—C10 | 1.382 (3) | C24—C25 | 1.370 (3) |
| C9—H9 | 0.9300 | C24—H24 | 0.9300 |
| C10—H10 | 0.9300 | C25—C26 | 1.376 (3) |
| C11—H11A | 0.9600 | C25—H25 | 0.9300 |
| C11—H11B | 0.9600 | C26—H26 | 0.9300 |
| C11—H11C | 0.9600 | | |

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| C1—N1—N2 | 109.46 (11) | C18—C12—C13 | 123.81 (13) |
| C1—N1—C5 | 123.58 (12) | C13—S1—C16 | 91.47 (12) |
| N2—N1—C5 | 118.79 (12) | C14—C13—C12 | 132.40 (16) |
| C3—N2—N1 | 106.84 (11) | C14—C13—S1 | 108.14 (15) |
| C3—N2—C11 | 123.14 (13) | C12—C13—S1 | 119.45 (12) |
| N1—N2—C11 | 118.55 (12) | C13—C14—C15 | 117.3 (3) |
| C12—N3—C2 | 125.74 (14) | C13—C14—H14 | 121.3 |
| C12—N3—H3 | 117.1 | C15—C14—H14 | 121.3 |
| C2—N3—H3 | 117.1 | C16—C15—C14 | 111.6 (3) |
| C17—N4—N5 | 111.56 (13) | C16—C15—H15 | 124.2 |
| C17—N4—C21 | 128.95 (13) | C14—C15—H15 | 124.2 |
| N5—N4—C21 | 119.43 (12) | C15—C16—S1 | 111.5 (3) |
| C19—N5—N4 | 106.83 (12) | C15—C16—H16 | 124.2 |
| O1—C1—N1 | 124.12 (14) | S1—C16—H16 | 124.2 |
| O1—C1—C2 | 131.66 (14) | C15′—C14′—H14′ | 122.8 |
| N1—C1—C2 | 104.21 (12) | C16′—C15′—C14′ | 111.7 (12) |
| C3—C2—N3 | 125.48 (14) | C16′—C15′—H15′ | 124.1 |
| C3—C2—C1 | 109.25 (13) | C14′—C15′—H15′ | 124.1 |
| N3—C2—C1 | 125.25 (13) | C15′—C16′—S1′ | 112.5 (11) |
| C2—C3—N2 | 109.66 (13) | C15′—C16′—H16′ | 123.7 |
| C2—C3—C4 | 128.65 (15) | S1′—C16′—H16′ | 123.7 |
| N2—C3—C4 | 121.65 (14) | O2—C17—N4 | 125.97 (15) |
| C3—C4—H4A | 109.5 | O2—C17—C18 | 128.66 (14) |

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| C3—C4—H4B | 109.5 | N4—C17—C18 | 105.36 (12) |
| H4A—C4—H4B | 109.5 | C12—C18—C17 | 122.15 (13) |
| C3—C4—H4C | 109.5 | C12—C18—C19 | 132.96 (15) |
| H4A—C4—H4C | 109.5 | C17—C18—C19 | 104.85 (13) |
| H4B—C4—H4C | 109.5 | N5—C19—C18 | 111.29 (14) |
| C10—C5—C6 | 120.45 (17) | N5—C19—C20 | 119.07 (14) |
| C10—C5—N1 | 121.06 (15) | C18—C19—C20 | 129.57 (16) |
| C6—C5—N1 | 118.48 (15) | C19—C20—H20A | 109.5 |
| C7—C6—C5 | 119.67 (19) | C19—C20—H20B | 109.5 |
| C7—C6—H6 | 120.2 | H20A—C20—H20B | 109.5 |
| C5—C6—H6 | 120.2 | C19—C20—H20C | 109.5 |
| C8—C7—C6 | 119.8 (2) | H20A—C20—H20C | 109.5 |
| C8—C7—H7 | 120.1 | H20B—C20—H20C | 109.5 |
| C6—C7—H7 | 120.1 | C26—C21—C22 | 119.95 (16) |
| C7—C8—C9 | 120.6 (2) | C26—C21—N4 | 119.76 (15) |
| C7—C8—H8 | 119.7 | C22—C21—N4 | 120.29 (14) |
| C9—C8—H8 | 119.7 | C23—C22—C21 | 119.30 (16) |
| C8—C9—C10 | 120.4 (2) | C23—C22—H22 | 120.3 |
| C8—C9—H9 | 119.8 | C21—C22—H22 | 120.3 |
| C10—C9—H9 | 119.8 | C24—C23—C22 | 120.84 (18) |
| C5—C10—C9 | 119.1 (2) | C24—C23—H23 | 119.6 |
| C5—C10—H10 | 120.5 | C22—C23—H23 | 119.6 |
| C9—C10—H10 | 120.5 | C25—C24—C23 | 119.24 (18) |
| N2—C11—H11A | 109.5 | C25—C24—H24 | 120.4 |
| N2—C11—H11B | 109.5 | C23—C24—H24 | 120.4 |
| H11A—C11—H11B | 109.5 | C24—C25—C26 | 121.12 (17) |
| N2—C11—H11C | 109.5 | C24—C25—H25 | 119.4 |
| H11A—C11—H11C | 109.5 | C26—C25—H25 | 119.4 |
| H11B—C11—H11C | 109.5 | C25—C26—C21 | 119.55 (17) |
| N3—C12—C18 | 118.10 (14) | C25—C26—H26 | 120.2 |
| N3—C12—C13 | 118.08 (14) | C21—C26—H26 | 120.2 |

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| C1—N1—N2—C3 | 7.51 (15) | N3—C12—C13—S1 | −109.04 (14) |
| C5—N1—N2—C3 | 157.23 (12) | C18—C12—C13—S1 | 69.48 (18) |
| C1—N1—N2—C11 | 152.10 (15) | C16—S1—C13—C14 | 0.23 (16) |
| C5—N1—N2—C11 | −58.19 (19) | C16—S1—C13—C12 | 179.22 (18) |
| C17—N4—N5—C19 | −2.41 (18) | C12—C13—C14—C15 | −179.3 (2) |
| C21—N4—N5—C19 | −179.86 (14) | S1—C13—C14—C15 | −0.51 (16) |
| N2—N1—C1—O1 | 174.18 (15) | C13—C14—C15—C16 | 0.6 (2) |
| C5—N1—C1—O1 | 26.2 (2) | C14—C15—C16—S1 | −0.4 (2) |
| N2—N1—C1—C2 | −4.47 (15) | C13—S1—C16—C15 | 0.1 (2) |
| C5—N1—C1—C2 | −152.43 (14) | C14′—C15′—C16′—S1′ | −1.0 (5) |
| C12—N3—C2—C3 | 97.57 (19) | N5—N4—C17—O2 | −175.43 (15) |
| C12—N3—C2—C1 | −84.5 (2) | C21—N4—C17—O2 | 1.7 (3) |
| O1—C1—C2—C3 | −178.69 (17) | N5—N4—C17—C18 | 3.33 (16) |
| N1—C1—C2—C3 | −0.18 (16) | C21—N4—C17—C18 | −179.53 (14) |
| O1—C1—C2—N3 | 3.1 (3) | N3—C12—C18—C17 | 4.9 (2) |
| N1—C1—C2—N3 | −178.36 (13) | C13—C12—C18—C17 | −173.64 (14) |

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| N3—C2—C3—N2 | −176.91 (13) | N3—C12—C18—C19 | −172.35 (16) |
| C1—C2—C3—N2 | 4.92 (17) | C13—C12—C18—C19 | 9.1 (3) |
| N3—C2—C3—C4 | 5.7 (3) | O2—C17—C18—C12 | −2.1 (3) |
| C1—C2—C3—C4 | −172.46 (16) | N4—C17—C18—C12 | 179.21 (14) |
| N1—N2—C3—C2 | −7.60 (16) | O2—C17—C18—C19 | 175.83 (16) |
| C11—N2—C3—C2 | −150.16 (14) | N4—C17—C18—C19 | −2.88 (16) |
| N1—N2—C3—C4 | 170.00 (14) | N4—N5—C19—C18 | 0.41 (18) |
| C11—N2—C3—C4 | 27.4 (2) | N4—N5—C19—C20 | 177.69 (15) |
| C1—N1—C5—C10 | 117.51 (17) | C12—C18—C19—N5 | 179.15 (16) |
| N2—N1—C5—C10 | −27.7 (2) | C17—C18—C19—N5 | 1.57 (18) |
| C1—N1—C5—C6 | −63.0 (2) | C12—C18—C19—C20 | 2.2 (3) |
| N2—N1—C5—C6 | 151.78 (13) | C17—C18—C19—C20 | −175.35 (18) |
| C10—C5—C6—C7 | −0.2 (2) | C17—N4—C21—C26 | −158.43 (15) |
| N1—C5—C6—C7 | −179.70 (14) | N5—N4—C21—C26 | 18.5 (2) |
| C5—C6—C7—C8 | 1.3 (3) | C17—N4—C21—C22 | 21.8 (2) |
| C6—C7—C8—C9 | −0.7 (3) | N5—N4—C21—C22 | −161.24 (15) |
| C7—C8—C9—C10 | −1.0 (3) | C26—C21—C22—C23 | 0.1 (3) |
| C6—C5—C10—C9 | −1.4 (3) | N4—C21—C22—C23 | 179.81 (15) |
| N1—C5—C10—C9 | 178.03 (16) | C21—C22—C23—C24 | 0.3 (3) |
| C8—C9—C10—C5 | 2.0 (3) | C22—C23—C24—C25 | −0.4 (3) |
| C2—N3—C12—C18 | −174.54 (14) | C23—C24—C25—C26 | 0.2 (3) |
| C2—N3—C12—C13 | 4.1 (2) | C24—C25—C26—C21 | 0.1 (3) |
| N3—C12—C13—C14 | 69.7 (2) | C22—C21—C26—C25 | −0.2 (2) |
| C18—C12—C13—C14 | −111.8 (2) | N4—C21—C26—C25 | −179.99 (15) |

*Hydrogen-bond geometry (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N3—H3···O2 | 0.86 | 1.96 | 2.6631 (18) | 138 |