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# *N*′-[(1*Z*)-1-(3-Methyl-5-oxo-1-phenyl-4,5-dihydro-1*H*-pyrazol-4-ylidene)ethyl]-2-[(4-methylphenyl)-sulfanyl]acetohydrazide

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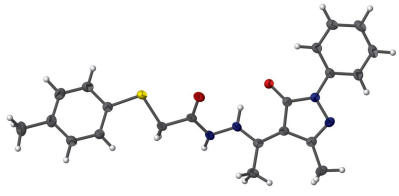
**CCDC reference**: 1586428

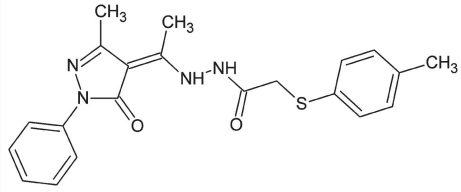
**Structural data**: full structural data are available from iucrdata.iucr.org

In the title compound, $C_{21}H_{22}N_4O_2S$, the dihedral angle between the pyrazole ring and adjacent benzene ring is 6.4 (1)°. The molecular conformation is influenced by intramolecular N—H···O and C—H···O hydrogen bonds. In the crystal, N—H···O hydrogen bonds plus C—H···$\pi$ and $\pi$–$\pi$ stacking interactions form chains extending in the *a*-axis direction. The chains are linked by complementary pairs of C—H···$\pi$ interactions.

**3D view**



**Chemical scheme**




## Structure description

Pyrazolone derivatives are important components of numerous pharmaceuticals, agrochemicals, dyes and pigments, chelating and extracting agents (*e.g.* Himly *et al.*, 2003; Shweta *et al.*, 2013). As part of our studies in this area, we now describe the synthesis and structure of the title compound. A related compound, (*Z*)-4-[1-(4-acetylanilino) ethylidene]-3-methyl-1-phenyl-1*H*-pyrazol-5(4*H*)-one derived from acyl pyrazolone and aromatic amine was reported to possess the keto–amine tautomer in the solid state (Mahfouz *et al.* 2015).

The conformation of the substituents on the 5-membered heterocyclic ring in the title compound is determined, in part, by the intramolecular N3—H3*A*···O1 hydrogen bond and, to a lesser extent, the intramolecular C2—H2···O1 hydrogen bond (Table 1 and Fig. 1). The dihedral angle between the mean planes of the C1–C6 and the N1/N2/C7–C9 rings is thus 6.4 (1)°, while that between the latter ring and the C15–C20 ring is 2.4 (1)°.

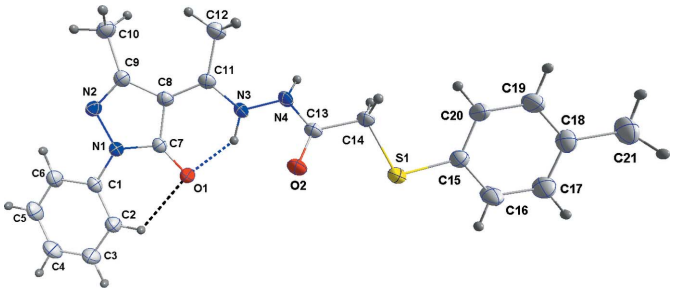



**Figure 1**
The molecular structure, with 50% probability displacement ellipsoids. The intramolecular N—H···O and C—H···O hydrogen bonds are shown as blue and black dashed lines, respectively.

Despite this, the molecule is not entirely planar as indicated by the C11—N3—N4—C13 torsion angle of 138.79 (19)°.

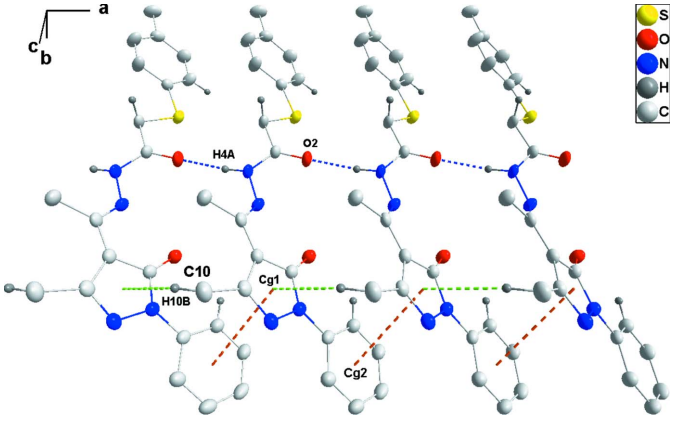



**Figure 2**
Plan view of the packing, showing the layers formed by intermolecular N—H···O hydrogen bonds (blue dashed lines) and C—H···$\pi$ and $\pi$–$\pi$ stacking interactions (green and orange dashed lines respectively).

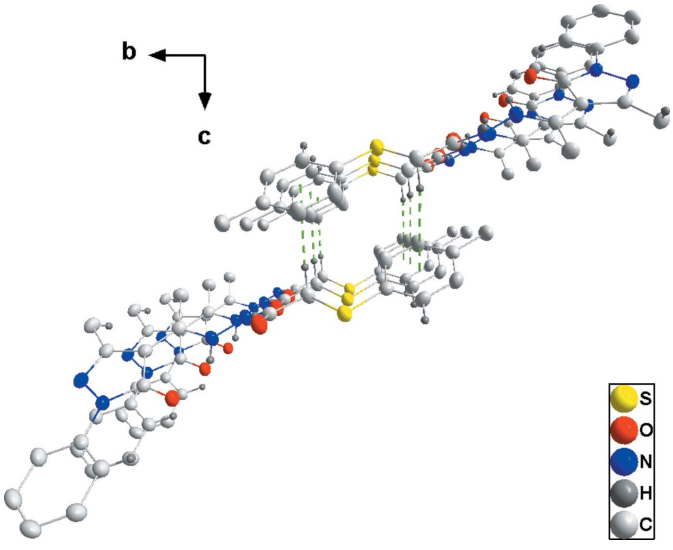



**Figure 3**
Elevation view of the packing along the *a*-axis direction, showing the connecting of two layers through C—H···$\pi$ interactions.

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

*Cg*1 and *Cg*3 are the centroids of the N1/N2/C7–C9 and C15–C20 rings, respectively.

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N3—H3*A*···O1 | 0.95 (3) | 1.82 (3) | 2.627 (2) | 141 (2) |
| N4—H4*A*···O2$^{i}$ | 0.90 (3) | 1.96 (3) | 2.858 (2) | 174 (2) |
| C2—H2···O1 | 0.96 (2) | 2.30 (2) | 2.937 (2) | 123.1 (18) |
| C10—H10*B*···*Cg*1$^{i}$ | 0.99 (3) | 2.80 (3) | 3.740 (2) | 159 (2) |
| C14—H14*A*···*Cg*3$^{ii}$ | 1.00 (2) | 2.99 (2) | 3.947 (3) | 161 (2) |
| C16—H16···O2$^{iii}$ | 0.94 (3) | 2.65 (3) | 3.436 (3) | 143 (2) |

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

**Table 2**
Experimental details.

| | |
|---|---|
| Crystal data | |
| Chemical formula | $C_{21}H_{22}N_4O_2S$ |
| $M_r$ | 394.48 |
| Crystal system, space group | Monoclinic, $P2_1/n$ |
| Temperature (K) | 150 |
| *a*, *b*, *c* (Å) | 4.8687 (2), 46.7634 (16), 8.4173 (3) |
| $\beta$ (°) | 100.232 (1) |
| *V* (Å$^3$) | 1885.95 (12) |
| *Z* | 4 |
| Radiation type | Cu $K\alpha$ |
| $\mu$ (mm$^{-1}$) | 1.73 |
| Crystal size (mm) | 0.19 × 0.08 × 0.04 |
| | |
| Data collection | |
| Diffractometer | Bruker D8 VENTURE PHOTON 100 CMOS |
| Absorption correction | Multi-scan (*SADABS*; Bruker, 2016) |
| $T_{min}$, $T_{max}$ | 0.78, 0.94 |
| No. of measured, independent and observed [$I > 2\sigma(I)$] reflections | 16199, 3723, 3404 |
| $R_{int}$ | 0.044 |
| (sin $\theta/\lambda)_{max}$ (Å$^{-1}$) | 0.625 |
| | |
| Refinement | |
| $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S* | 0.044, 0.103, 1.12 |
| No. of reflections | 3723 |
| No. of parameters | 341 |
| H-atom treatment | All H-atom parameters refined |
| $\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å$^{-3}$) | 0.23, −0.27 |

Computer programs: *APEX3* and *SAINT* (Bruker, 2016), *SHELXT* (Sheldrick, 2015*a*), *SHELXL2014* (Sheldrick, 2015*b*), *DIAMOND* (Brandenburg & Putz, 2012) and *SHELXTL* (Sheldrick, 2008).

In the crystal, N4—H4*A*···O2 hydrogen bonds accompanied by C—H···$\pi$ (C10—H10*B*···*Cg*1; Table 1 and Fig. 2) and $\pi$–$\pi$-stacking interactions [*Cg*1···*Cg*2($-1+x$, y, *z*) = 3.667 (1) Å, *Cg*1 and *Cg*2 are the centroids of the N1/N2/C7–C9 and C1–C6 rings, respectively] form chains propagating along the *a*-axis direction (Fig. 2). These chains are linked through pairwise C—H···$\pi$ [C14—H14*A*···*Cg*3; *Cg*3 is the centroid of the C15–C20 ring at $-x, -y+1, -z$] interactions (Fig. 3 and Table 1).

## Synthesis and crystallization

The title compound was obtained by refluxing equimolar quantities of 4-acetyl-3-methyl-1-phenyl-2-pyrazolin-5-one

(1.081 g m, 5 mmol) and 2-(4-tolylthio)acethydrazide (0.981 g m, 5 mmol) in 30 ml ethanol for 2 h. On cooling, the yellow precipitate was collected by filtration and recrystallized from dimethylformamide (DMF) solution as colourless plates. Yield (89%); m.p. 443–445 K; IR (KBr, $cm^{-1}$); 3232 (NH), 1656,1633 (2 C═O).

## Refinement

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

## Acknowledgements

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# full crystallographic data

*IUCrData* (2017). **2**, x171666 [https://doi.org/10.1107/S2414314617016662]

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**N′-[(1Z)-1-(3-Methyl-5-oxo-1-phenyl-4,5-dihydro-1H-pyrazol-4-ylidene)ethyl]-2-[(4-methylphenyl)sulfanyl]acetohydrazide**

*Crystal data*

$C_{21}H_{22}N_4O_2S$
$M_r$ = 394.48
Monoclinic, $P2_1/n$
$a$ = 4.8687 (2) Å
$b$ = 46.7634 (16) Å
$c$ = 8.4173 (3) Å
$\beta$ = 100.232 (1)°
$V$ = 1885.95 (12) Å$^3$
$Z$ = 4
$F(000)$ = 832
$D_x$ = 1.389 Mg m$^{-3}$
Cu $K\alpha$ radiation, $\lambda$ = 1.54178 Å
Cell parameters from 9883 reflections
$\theta$ = 3.8–74.5°
$\mu$ = 1.73 mm$^{-1}$
$T$ = 150 K
Plate, colourless
0.19 × 0.08 × 0.04 mm

*Data collection*

Bruker D8 VENTURE PHOTON 100 CMOS diffractometer
Radiation source: INCOATEC I$\mu$S micro-focus source
Mirror monochromator
Detector resolution: 10.4167 pixels mm$^{-1}$
$\omega$ scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2016)
$T_{min}$ = 0.78, $T_{max}$ = 0.94
16199 measured reflections
3723 independent reflections
3404 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.044
$\theta_{max}$ = 74.5°, $\theta_{min}$ = 3.8°
$h$ = −6→5
$k$ = −57→53
$l$ = −10→9

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.044
$wR(F^2)$ = 0.103
$S$ = 1.12
3723 reflections
341 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: difference Fourier map
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.023P)^2 + 1.718P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.002
$\Delta\rho_{max}$ = 0.23 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.27 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 $F^2 > 2\text{sigma}(F^2)$ 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* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| S1 | 0.23101 (10) | 0.51189 (2) | 0.34557 (6) | 0.03032 (14) |
| O1 | 0.4863 (3) | 0.63157 (3) | 0.66802 (17) | 0.0278 (3) |
| O2 | 0.3695 (3) | 0.57155 (3) | 0.37885 (19) | 0.0324 (3) |
| N1 | 0.4559 (3) | 0.68151 (3) | 0.69106 (19) | 0.0229 (3) |
| N2 | 0.2746 (3) | 0.70331 (3) | 0.6214 (2) | 0.0247 (3) |
| N3 | 0.0537 (3) | 0.61217 (3) | 0.4649 (2) | 0.0268 (4) |
| H3A | 0.222 (6) | 0.6101 (5) | 0.541 (3) | 0.043 (7)* |
| N4 | −0.0633 (3) | 0.58791 (3) | 0.3844 (2) | 0.0262 (4) |
| H4A | −0.243 (6) | 0.5838 (5) | 0.388 (3) | 0.036 (6)* |
| C1 | 0.6842 (4) | 0.68887 (4) | 0.8128 (2) | 0.0231 (4) |
| C2 | 0.8821 (4) | 0.66859 (4) | 0.8780 (2) | 0.0275 (4) |
| H2 | 0.869 (5) | 0.6493 (5) | 0.840 (3) | 0.034 (6)* |
| C3 | 1.1042 (4) | 0.67684 (5) | 0.9954 (3) | 0.0312 (4) |
| H3 | 1.244 (6) | 0.6623 (6) | 1.040 (3) | 0.045 (7)* |
| C4 | 1.1317 (5) | 0.70485 (5) | 1.0504 (3) | 0.0337 (5) |
| H4 | 1.298 (5) | 0.7096 (5) | 1.136 (3) | 0.037 (6)* |
| C5 | 0.9319 (5) | 0.72481 (5) | 0.9863 (3) | 0.0335 (5) |
| H5 | 0.944 (5) | 0.7449 (5) | 1.026 (3) | 0.039 (6)* |
| C6 | 0.7097 (4) | 0.71708 (4) | 0.8682 (3) | 0.0295 (4) |
| H6 | 0.569 (5) | 0.7305 (5) | 0.821 (3) | 0.035 (6)* |
| C7 | 0.3680 (4) | 0.65506 (4) | 0.6301 (2) | 0.0224 (4) |
| C8 | 0.1170 (4) | 0.66065 (4) | 0.5138 (2) | 0.0227 (4) |
| C9 | 0.0774 (4) | 0.69108 (4) | 0.5178 (2) | 0.0233 (4) |
| C10 | −0.1466 (4) | 0.70947 (5) | 0.4262 (3) | 0.0301 (4) |
| H10A | −0.149 (6) | 0.7090 (6) | 0.308 (3) | 0.046 (7)* |
| H10B | −0.334 (6) | 0.7035 (6) | 0.443 (3) | 0.047 (7)* |
| H10C | −0.110 (5) | 0.7297 (6) | 0.467 (3) | 0.043 (7)* |
| C11 | −0.0348 (4) | 0.63867 (4) | 0.4278 (2) | 0.0234 (4) |
| C12 | −0.2844 (4) | 0.64281 (5) | 0.2995 (3) | 0.0310 (4) |
| H12A | −0.263 (7) | 0.6320 (7) | 0.200 (4) | 0.071 (10)* |
| H12B | −0.449 (8) | 0.6345 (7) | 0.331 (4) | 0.078 (10)* |
| H12C | −0.326 (7) | 0.6624 (8) | 0.279 (4) | 0.081 (11)* |
| C13 | 0.1168 (4) | 0.56754 (4) | 0.3541 (2) | 0.0242 (4) |
| C14 | −0.0179 (4) | 0.54011 (4) | 0.2839 (3) | 0.0277 (4) |
| H14A | −0.052 (5) | 0.5424 (5) | 0.164 (3) | 0.029 (6)* |

| | | | | |
|---|---|---|---|---|
| H14B | −0.189 (5) | 0.5365 (5) | 0.317 (3) | 0.036 (6)* |
| C15 | 0.0623 (4) | 0.48142 (4) | 0.2500 (2) | 0.0258 (4) |
| C16 | 0.1980 (5) | 0.45551 (5) | 0.2878 (3) | 0.0356 (5) |
| H16 | 0.366 (6) | 0.4553 (6) | 0.362 (3) | 0.052 (8)* |
| C17 | 0.0904 (5) | 0.43032 (5) | 0.2146 (3) | 0.0367 (5) |
| H17 | 0.191 (6) | 0.4126 (6) | 0.243 (3) | 0.044 (7)* |
| C18 | −0.1533 (5) | 0.43025 (4) | 0.1019 (2) | 0.0315 (4) |
| C19 | −0.2882 (5) | 0.45609 (5) | 0.0662 (3) | 0.0402 (5) |
| H19 | −0.460 (6) | 0.4568 (6) | −0.013 (3) | 0.051 (8)* |
| C20 | −0.1826 (5) | 0.48153 (5) | 0.1387 (3) | 0.0373 (5) |
| H20 | −0.279 (6) | 0.4986 (6) | 0.113 (3) | 0.054 (8)* |
| C21 | −0.2696 (7) | 0.40302 (5) | 0.0196 (3) | 0.0431 (6) |
| H21A | −0.323 (7) | 0.3891 (7) | 0.093 (4) | 0.074 (10)* |
| H21B | −0.123 (8) | 0.3934 (7) | −0.028 (4) | 0.077 (11)* |
| H21C | −0.433 (8) | 0.4066 (8) | −0.065 (5) | 0.087 (12)* |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| S1 | 0.0232 (2) | 0.0279 (3) | 0.0363 (3) | 0.00029 (18) | −0.00429 (19) | −0.00213 (19) |
| O1 | 0.0256 (7) | 0.0216 (7) | 0.0337 (8) | 0.0005 (5) | −0.0012 (6) | 0.0002 (5) |
| O2 | 0.0155 (7) | 0.0340 (8) | 0.0468 (9) | −0.0025 (5) | 0.0032 (6) | −0.0049 (6) |
| N1 | 0.0211 (8) | 0.0218 (7) | 0.0256 (8) | −0.0012 (6) | 0.0033 (6) | 0.0003 (6) |
| N2 | 0.0233 (8) | 0.0231 (8) | 0.0287 (9) | 0.0026 (6) | 0.0073 (7) | 0.0027 (6) |
| N3 | 0.0207 (8) | 0.0256 (8) | 0.0321 (9) | −0.0032 (6) | −0.0010 (7) | −0.0045 (7) |
| N4 | 0.0142 (8) | 0.0265 (8) | 0.0373 (10) | −0.0043 (6) | 0.0033 (7) | −0.0062 (7) |
| C1 | 0.0206 (9) | 0.0269 (9) | 0.0231 (10) | −0.0049 (7) | 0.0071 (7) | −0.0016 (7) |
| C2 | 0.0260 (10) | 0.0278 (10) | 0.0285 (10) | −0.0025 (8) | 0.0039 (8) | −0.0015 (8) |
| C3 | 0.0251 (10) | 0.0383 (11) | 0.0292 (11) | −0.0022 (8) | 0.0022 (8) | −0.0012 (8) |
| C4 | 0.0272 (11) | 0.0459 (12) | 0.0277 (11) | −0.0100 (9) | 0.0037 (9) | −0.0069 (9) |
| C5 | 0.0332 (11) | 0.0328 (11) | 0.0363 (12) | −0.0103 (9) | 0.0109 (9) | −0.0102 (9) |
| C6 | 0.0281 (10) | 0.0272 (10) | 0.0344 (11) | −0.0032 (8) | 0.0092 (9) | −0.0044 (8) |
| C7 | 0.0206 (9) | 0.0235 (9) | 0.0237 (9) | −0.0020 (7) | 0.0057 (7) | 0.0006 (7) |
| C8 | 0.0187 (9) | 0.0261 (9) | 0.0239 (9) | 0.0005 (7) | 0.0060 (7) | 0.0012 (7) |
| C9 | 0.0212 (9) | 0.0262 (9) | 0.0246 (10) | 0.0003 (7) | 0.0094 (7) | 0.0026 (7) |
| C10 | 0.0261 (10) | 0.0305 (11) | 0.0346 (12) | 0.0058 (8) | 0.0078 (9) | 0.0065 (8) |
| C11 | 0.0164 (8) | 0.0285 (9) | 0.0265 (10) | 0.0006 (7) | 0.0074 (7) | 0.0002 (7) |
| C12 | 0.0242 (10) | 0.0363 (11) | 0.0307 (11) | 0.0002 (8) | −0.0003 (9) | −0.0018 (9) |
| C13 | 0.0171 (9) | 0.0279 (9) | 0.0268 (10) | −0.0016 (7) | 0.0021 (7) | −0.0002 (7) |
| C14 | 0.0154 (9) | 0.0295 (10) | 0.0369 (12) | −0.0006 (7) | 0.0013 (8) | −0.0065 (8) |
| C15 | 0.0249 (9) | 0.0271 (10) | 0.0259 (10) | −0.0005 (7) | 0.0056 (8) | −0.0001 (7) |
| C16 | 0.0378 (12) | 0.0315 (11) | 0.0330 (12) | 0.0008 (9) | −0.0065 (10) | 0.0052 (9) |
| C17 | 0.0452 (13) | 0.0262 (10) | 0.0368 (12) | 0.0037 (9) | 0.0022 (10) | 0.0049 (8) |
| C18 | 0.0410 (12) | 0.0272 (10) | 0.0269 (10) | −0.0028 (9) | 0.0079 (9) | −0.0007 (8) |
| C19 | 0.0380 (12) | 0.0323 (11) | 0.0437 (14) | −0.0003 (9) | −0.0109 (11) | −0.0037 (9) |
| C20 | 0.0299 (11) | 0.0275 (11) | 0.0494 (14) | 0.0037 (9) | −0.0068 (10) | −0.0049 (9) |
| C21 | 0.0645 (17) | 0.0283 (11) | 0.0348 (13) | −0.0053 (11) | 0.0037 (12) | −0.0030 (9) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| S1—C15 | 1.765 (2) | C8—C9 | 1.437 (3) |
| S1—C14 | 1.805 (2) | C9—C10 | 1.492 (3) |
| O1—C7 | 1.255 (2) | C10—H10A | 0.99 (3) |
| O2—C13 | 1.225 (2) | C10—H10B | 0.99 (3) |
| N1—C7 | 1.378 (2) | C10—H10C | 1.01 (3) |
| N1—N2 | 1.407 (2) | C11—C12 | 1.488 (3) |
| N1—C1 | 1.414 (2) | C12—H12A | 1.00 (3) |
| N2—C9 | 1.308 (3) | C12—H12B | 0.97 (4) |
| N3—C11 | 1.331 (2) | C12—H12C | 0.95 (4) |
| N3—N4 | 1.391 (2) | C13—C14 | 1.512 (3) |
| N3—H3A | 0.95 (3) | C14—H14A | 1.00 (2) |
| N4—C13 | 1.349 (2) | C14—H14B | 0.94 (3) |
| N4—H4A | 0.90 (3) | C15—C20 | 1.380 (3) |
| C1—C2 | 1.393 (3) | C15—C16 | 1.390 (3) |
| C1—C6 | 1.397 (3) | C16—C17 | 1.388 (3) |
| C2—C3 | 1.384 (3) | C16—H16 | 0.94 (3) |
| C2—H2 | 0.96 (2) | C17—C18 | 1.382 (3) |
| C3—C4 | 1.388 (3) | C17—H17 | 0.97 (3) |
| C3—H3 | 0.98 (3) | C18—C19 | 1.383 (3) |
| C4—C5 | 1.387 (3) | C18—C21 | 1.511 (3) |
| C4—H4 | 1.01 (3) | C19—C20 | 1.393 (3) |
| C5—C6 | 1.381 (3) | C19—H19 | 0.97 (3) |
| C5—H5 | 1.00 (2) | C20—H20 | 0.93 (3) |
| C6—H6 | 0.96 (3) | C21—H21A | 0.96 (4) |
| C7—C8 | 1.448 (3) | C21—H21B | 0.99 (4) |
| C8—C11 | 1.391 (3) | C21—H21C | 0.98 (4) |
| | | | |
| C15—S1—C14 | 103.00 (9) | H10B—C10—H10C | 109 (2) |
| C7—N1—N2 | 111.40 (15) | N3—C11—C8 | 116.50 (17) |
| C7—N1—C1 | 129.83 (16) | N3—C11—C12 | 118.68 (18) |
| N2—N1—C1 | 118.70 (15) | C8—C11—C12 | 124.83 (18) |
| C9—N2—N1 | 107.04 (15) | C11—C12—H12A | 110.4 (19) |
| C11—N3—N4 | 123.90 (17) | C11—C12—H12B | 111 (2) |
| C11—N3—H3A | 117.1 (15) | H12A—C12—H12B | 104 (3) |
| N4—N3—H3A | 118.5 (15) | C11—C12—H12C | 112 (2) |
| C13—N4—N3 | 116.36 (16) | H12A—C12—H12C | 113 (3) |
| C13—N4—H4A | 121.5 (16) | H12B—C12—H12C | 106 (3) |
| N3—N4—H4A | 118.3 (16) | O2—C13—N4 | 121.79 (17) |
| C2—C1—C6 | 119.79 (19) | O2—C13—C14 | 123.27 (17) |
| C2—C1—N1 | 121.30 (17) | N4—C13—C14 | 114.92 (16) |
| C6—C1—N1 | 118.91 (18) | C13—C14—S1 | 106.59 (13) |
| C3—C2—C1 | 119.33 (19) | C13—C14—H14A | 106.7 (13) |
| C3—C2—H2 | 119.8 (15) | S1—C14—H14A | 110.7 (13) |
| C1—C2—H2 | 120.9 (15) | C13—C14—H14B | 112.5 (15) |
| C2—C3—C4 | 121.2 (2) | S1—C14—H14B | 111.4 (15) |
| C2—C3—H3 | 118.4 (16) | H14A—C14—H14B | 109 (2) |

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| C4—C3—H3 | 120.4 (16) | C20—C15—C16 | 118.48 (19) |
| C5—C4—C3 | 119.1 (2) | C20—C15—S1 | 125.64 (16) |
| C5—C4—H4 | 123.2 (14) | C16—C15—S1 | 115.83 (16) |
| C3—C4—H4 | 117.7 (14) | C17—C16—C15 | 120.8 (2) |
| C6—C5—C4 | 120.6 (2) | C17—C16—H16 | 120.2 (17) |
| C6—C5—H5 | 118.6 (15) | C15—C16—H16 | 119.0 (17) |
| C4—C5—H5 | 120.8 (15) | C18—C17—C16 | 121.2 (2) |
| C5—C6—C1 | 119.9 (2) | C18—C17—H17 | 119.9 (16) |
| C5—C6—H6 | 122.5 (15) | C16—C17—H17 | 118.9 (16) |
| C1—C6—H6 | 117.5 (15) | C17—C18—C19 | 117.6 (2) |
| O1—C7—N1 | 126.39 (18) | C17—C18—C21 | 121.6 (2) |
| O1—C7—C8 | 128.62 (17) | C19—C18—C21 | 120.8 (2) |
| N1—C7—C8 | 104.99 (15) | C18—C19—C20 | 121.8 (2) |
| C11—C8—C9 | 133.06 (18) | C18—C19—H19 | 119.8 (16) |
| C11—C8—C7 | 121.66 (17) | C20—C19—H19 | 118.4 (16) |
| C9—C8—C7 | 105.27 (16) | C15—C20—C19 | 120.1 (2) |
| N2—C9—C8 | 111.30 (17) | C15—C20—H20 | 119.8 (18) |
| N2—C9—C10 | 118.37 (17) | C19—C20—H20 | 120.1 (18) |
| C8—C9—C10 | 130.34 (18) | C18—C21—H21A | 113 (2) |
| C9—C10—H10A | 112.6 (16) | C18—C21—H21B | 109 (2) |
| C9—C10—H10B | 111.7 (16) | H21A—C21—H21B | 104 (3) |
| H10A—C10—H10B | 107 (2) | C18—C21—H21C | 112 (2) |
| C9—C10—H10C | 107.2 (15) | H21A—C21—H21C | 108 (3) |
| H10A—C10—H10C | 109 (2) | H21B—C21—H21C | 109 (3) |

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| C7—N1—N2—C9 | −0.5 (2) | C7—C8—C9—N2 | 0.1 (2) |
| C1—N1—N2—C9 | −177.73 (15) | C11—C8—C9—C10 | −0.7 (3) |
| C11—N3—N4—C13 | 138.79 (19) | C7—C8—C9—C10 | −179.26 (19) |
| C7—N1—C1—C2 | 8.0 (3) | N4—N3—C11—C8 | −175.98 (17) |
| N2—N1—C1—C2 | −175.34 (16) | N4—N3—C11—C12 | 4.0 (3) |
| C7—N1—C1—C6 | −171.82 (18) | C9—C8—C11—N3 | −174.60 (19) |
| N2—N1—C1—C6 | 4.8 (2) | C7—C8—C11—N3 | 3.8 (3) |
| C6—C1—C2—C3 | −1.0 (3) | C9—C8—C11—C12 | 5.4 (3) |
| N1—C1—C2—C3 | 179.13 (18) | C7—C8—C11—C12 | −176.18 (18) |
| C1—C2—C3—C4 | 0.7 (3) | N3—N4—C13—O2 | −8.4 (3) |
| C2—C3—C4—C5 | 0.1 (3) | N3—N4—C13—C14 | 173.28 (17) |
| C3—C4—C5—C6 | −0.6 (3) | O2—C13—C14—S1 | 29.7 (2) |
| C4—C5—C6—C1 | 0.3 (3) | N4—C13—C14—S1 | −152.02 (15) |
| C2—C1—C6—C5 | 0.6 (3) | C15—S1—C14—C13 | −177.22 (14) |
| N1—C1—C6—C5 | −179.58 (18) | C14—S1—C15—C20 | 8.0 (2) |
| N2—N1—C7—O1 | 179.70 (17) | C14—S1—C15—C16 | −174.65 (17) |
| C1—N1—C7—O1 | −3.5 (3) | C20—C15—C16—C17 | 0.3 (3) |
| N2—N1—C7—C8 | 0.57 (19) | S1—C15—C16—C17 | −177.29 (18) |
| C1—N1—C7—C8 | 177.41 (17) | C15—C16—C17—C18 | 0.3 (4) |
| O1—C7—C8—C11 | 1.7 (3) | C16—C17—C18—C19 | −0.9 (3) |
| N1—C7—C8—C11 | −179.19 (16) | C16—C17—C18—C21 | 179.0 (2) |
| O1—C7—C8—C9 | −179.53 (18) | C17—C18—C19—C20 | 0.9 (4) |
| N1—C7—C8—C9 | −0.42 (19) | C21—C18—C19—C20 | −179.0 (2) |

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| N1—N2—C9—C8 | 0.2 (2) | C16—C15—C20—C19 | −0.3 (4) |
| N1—N2—C9—C10 | 179.68 (16) | S1—C15—C20—C19 | 177.05 (19) |
| C11—C8—C9—N2 | 178.71 (19) | C18—C19—C20—C15 | −0.3 (4) |

*Hydrogen-bond geometry (Å, º)*

Cg1 and Cg3 are the centroids of the N1/N2/C7–C9 and C15–C20 rings, respectively.

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N3—H3*A*···O1 | 0.95 (3) | 1.82 (3) | 2.627 (2) | 141 (2) |
| N4—H4*A*···O2$^{i}$ | 0.90 (3) | 1.96 (3) | 2.858 (2) | 174 (2) |
| C2—H2···O1 | 0.96 (2) | 2.30 (2) | 2.937 (2) | 123.1 (18) |
| C10—H10*B*···*Cg*1$^{i}$ | 0.99 (3) | 2.80 (3) | 3.740 (2) | 159 (2) |
| C14—H14*A*···*Cg*3$^{ii}$ | 1.00 (2) | 2.99 (2) | 3.947 (3) | 161 (2) |
| C16—H16···O2$^{iii}$ | 0.94 (3) | 2.65 (3) | 3.436 (3) | 143 (2) |

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