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# (4*Z*)-4-[1-(2-Aminoanilino)ethylidene]-3-methyl-1-phenyl-4,5-dihydro-1*H*-pyrazol-5-one

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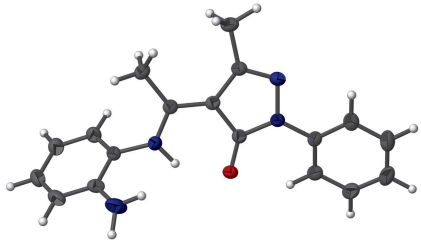
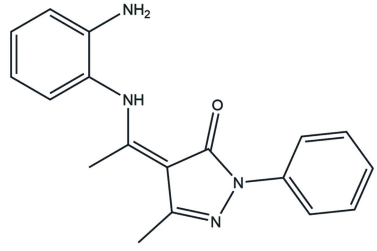
**Structural data**: full structural data are available from iucrdata.iucr.org

The conformation of the title compound, $C_{18}H_{18}N_4O$, is partly determined by an intramolecular N—H···O hydrogen bond that imposes planarity on the central aminoethylidene-3-methylpyrazol-5-one segment of the molecule. In the crystal, N—H···O hydrogen and N—H···N hydrogen bonds both form centrosymmetric dimers that enclose $R_2^2(18)$ rings. These, together with C—H···N and $\pi$–$\pi$ stacking interactions between centrosymmetrically related pyrazalone rings, stack the molecules along the *b*-axis direction.

**3D view**



**Chemical scheme**




## Structure description

Pyrazole derivatives are known to possess a broad spectrum of biological activities, acting as cannabinoid receptor antagonists (Lan *et al.*, 1999), antibacterial (Tanitame *et al.*, 2004), anti-inflammatory and antimicrobial agents (Bekhit & Abdel-Aziem, 2004). In a continuation of our research using acetoacetyl pyrazole as starting material in the synthesis of several heterocyclic systems with potent pharmacological properties (Djerrari *et al.*, 2001,2003), we report in this work the crystal structure of the title pyrazolone derivative.

The conformation of the title molecule is partially determined by an intramolecular N3—H3···O1 hydrogen bond (Table 1, Figs. 1 and 2). This ensures the planarity of the central C13/N3/C12(C11)[N1,N2,C1(C10)C2,C3(O1)] section of the molecule, r.m.s. deviation 0.0403 Å. The dihedral angle between the mean planes of the N1/N2/C1–C3 and C4–C9 rings is 21.31 (4)° while that between the former ring and the C13—C18 ring is 62.60 (5)°.

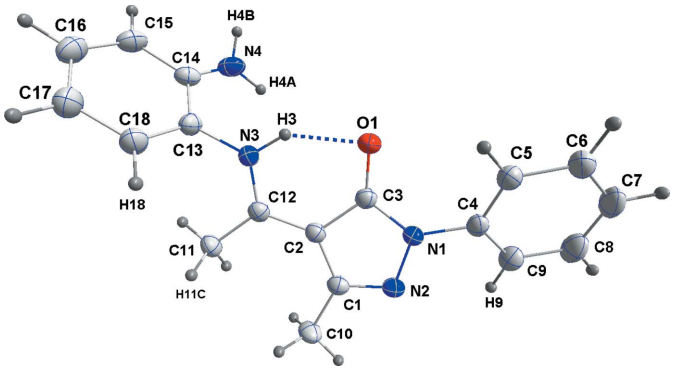



**Figure 1**
The title molecule with the labelling scheme and 50% probability displacement ellipsoids. The intramolecular hydrogen bond is shown as a dashed line.

In the crystal, the molecules form centrosymmetric dimers through pairwise N4—H4*B*···O1$^{ii}$ hydrogen bonds, Table 1. N1—H4*A*···N2$^{i}$ hydrogen bonds also form inversion dimers with both sets of dimers forming $R_2^2(18)$ ring motifs. The dimers stack along the *b*-axis direction aided by C9—H9···N4$^{i}$, C11—H11*C*···N1$^{iii}$ and C18—H18···N2$^{iii}$ hydrogen bonds and offset $\pi$–$\pi$-stacking interactions [*Cg*1···*Cg*1$^{iv}$ = 3.758 (1) Å; symmetry code: (iv) $1-x, 1-y, 1-z$] between pairs of centrosymmetrically related pyrazolone rings (Table 1, Figs. 2 and 3). The individual stacks show only normal van der Waals contacts between them.

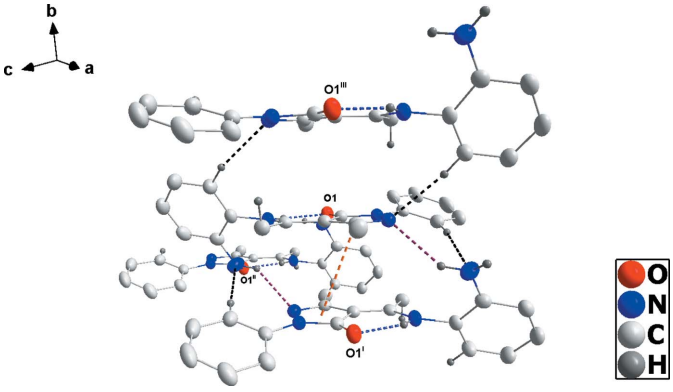



**Figure 2**
Detail of the intra- and intermolecular molecular interactions (dashed lines: N—H···O, blue; N—H···N, purple; C—H···O; black; $\pi$–$\pi$ stacking, orange). For symmetry codes, see Table 1.

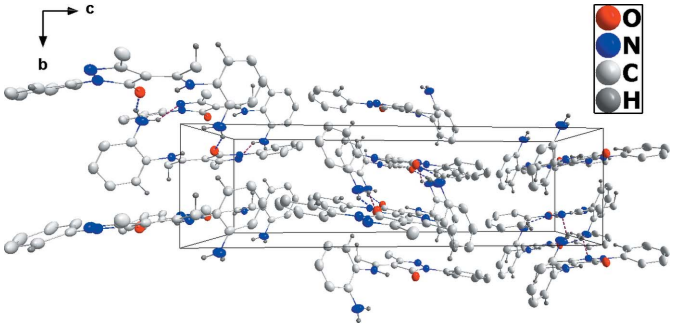



**Figure 3**
Crystal packing, viewed along the *a* axis (the colour codes for the hydrogen bonds are given in Fig. 2).

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

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N3—H3···O1 | 0.955 (18) | 1.863 (18) | 2.6965 (14) | 144.3 (15) |
| N4—H4*A*···N2$^{i}$ | 0.92 (2) | 2.47 (2) | 3.2542 (17) | 144.1 (16) |
| N4—H4*B*···O1$^{ii}$ | 0.93 (2) | 2.14 (2) | 3.0090 (16) | 153.3 (17) |
| C9—H9···N4$^{i}$ | 1.008 (17) | 2.567 (17) | 3.571 (2) | 173.7 (13) |
| C11—H11*C*···N1$^{iii}$ | 0.98 (2) | 2.68 (2) | 3.5669 (19) | 152.0 (16) |
| C18—H18···N2$^{iii}$ | 0.997 (17) | 2.439 (17) | 3.3984 (18) | 161.2 (13) |

Symmetry codes: (i) $-x+1, -y+1, -z+1$; (ii) $-x, -y+1, -z+1$; (iii) $-x+1, -y+2, -z+1$.

**Table 2**
Experimental details.

| | |
|---|---|
| Crystal data | |
| Chemical formula | $C_{18}H_{18}N_4O$ |
| $M_r$ | 306.36 |
| Crystal system, space group | Monoclinic, $P2_1/c$ |
| Temperature (K) | 150 |
| *a*, *b*, *c* (Å) | 8.6575 (2), 7.1749 (1), 25.3062 (5) |
| $\beta$ (°) | 93.782 (1) |
| *V* (Å$^3$) | 1568.51 (5) |
| *Z* | 4 |
| Radiation type | Cu $K\alpha$ |
| $\mu$ (mm$^{-1}$) | 0.67 |
| Crystal size (mm) | 0.19 × 0.05 × 0.05 |
| | |
| Data collection | |
| Diffractometer | Bruker D8 VENTURE PHOTON 100 CMOS |
| Absorption correction | Multi-scan (*SADABS*; Bruker, 2016) |
| $T_{min}$, $T_{max}$ | 0.87, 0.97 |
| No. of measured, independent and observed [$I > 2\sigma(I)$] reflections | 11756, 3032, 2596 |
| $R_{int}$ | 0.035 |
| (sin $\theta/\lambda)_{max}$ (Å$^{-1}$) | 0.618 |
| | |
| Refinement | |
| $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S* | 0.038, 0.096, 1.04 |
| No. of reflections | 3032 |
| No. of parameters | 281 |
| H-atom treatment | All H-atom parameters refined |
| $\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å$^{-3}$) | 0.29, −0.18 |

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

## Synthesis and crystallization

To a solution of acetoacetyl pyrazole (0.001 mol) in 40 ml of ethanol was added *o*-phenylenediamine (0.002 mol). The reaction mixture was refluxed for 2 h. After cooling, the solvent was removed under reduced pressure. The residue obtained was recrystallized from ethanol to afford colourless block-like crystals of the title compound (m.p. 485–487 K, yield: 80%).

## 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**, x170256 [https://doi.org/10.1107/S2414314617002565]

## (4*Z*)-4-[1-(2-Aminoanilino)ethylidene]-3-methyl-1-phenyl-4,5-dihydro-1*H*-pyrazol-5-one

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**(4*Z*)-4-[1-(2-Aminoanilino)ethylidene]-3-methyl-1-phenyl-4,5-dihydro-1*H*-pyrazol-5-one**

*Crystal data*

$C_{18}H_{18}N_4O$
$M_r$ = 306.36
Monoclinic, $P2_1/c$
$a$ = 8.6575 (2) Å
$b$ = 7.1749 (1) Å
$c$ = 25.3062 (5) Å
$\beta$ = 93.782 (1)°
$V$ = 1568.51 (5) Å$^3$
$Z$ = 4
$F(000)$ = 648
$D_x$ = 1.297 Mg m$^{-3}$
Cu $K\alpha$ radiation, $\lambda$ = 1.54178 Å
Cell parameters from 8108 reflections
$\theta$ = 5.1–72.4°
$\mu$ = 0.67 mm$^{-1}$
$T$ = 150 K
Column, colourless
0.19 × 0.05 × 0.05 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)
$T_{min}$ = 0.87, $T_{max}$ = 0.97
11756 measured reflections
3032 independent reflections
2596 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.035
$\theta_{max}$ = 72.4°, $\theta_{min}$ = 5.1°
$h$ = −10→10
$k$ = −8→8
$l$ = −31→30

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.038
$wR(F^2)$ = 0.096
$S$ = 1.04
3032 reflections
281 parameters
0 restraints
Hydrogen site location: difference Fourier map
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0455P)^2 + 0.4468P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.29 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.18 e Å$^{-3}$
Extinction correction: *SHELXL2014* (Sheldrick, 2015*b*), $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.0050 (4)

*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* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| O1 | 0.23306 (10) | 0.69400 (14) | 0.45467 (4) | 0.0305 (2) |
| N1 | 0.48083 (12) | 0.71074 (15) | 0.42251 (4) | 0.0248 (2) |
| N2 | 0.63327 (12) | 0.73552 (16) | 0.44323 (4) | 0.0270 (3) |
| N3 | 0.25320 (13) | 0.75094 (16) | 0.56022 (4) | 0.0276 (3) |
| C1 | 0.62652 (14) | 0.75905 (17) | 0.49448 (5) | 0.0248 (3) |
| C2 | 0.47020 (14) | 0.74833 (17) | 0.50980 (5) | 0.0234 (3) |
| C3 | 0.37694 (14) | 0.71531 (17) | 0.46141 (5) | 0.0241 (3) |
| H3 | 0.203 (2) | 0.721 (2) | 0.5265 (7) | 0.044 (5)* |
| C4 | 0.45262 (15) | 0.68737 (17) | 0.36708 (5) | 0.0258 (3) |
| H4A | 0.132 (2) | 0.447 (3) | 0.5721 (8) | 0.051 (5)* |
| H4B | −0.032 (2) | 0.404 (3) | 0.5913 (8) | 0.057 (6)* |
| N4 | 0.05992 (15) | 0.47138 (18) | 0.59596 (6) | 0.0405 (3) |
| C5 | 0.30760 (17) | 0.7256 (2) | 0.34286 (5) | 0.0316 (3) |
| H5 | 0.221 (2) | 0.771 (2) | 0.3632 (7) | 0.040 (4)* |
| C6 | 0.28126 (19) | 0.6947 (2) | 0.28880 (6) | 0.0406 (4) |
| H6 | 0.179 (2) | 0.722 (3) | 0.2718 (7) | 0.047 (5)* |
| C7 | 0.3984 (2) | 0.6291 (3) | 0.25907 (6) | 0.0451 (4) |
| H7 | 0.379 (2) | 0.604 (3) | 0.2209 (8) | 0.057 (5)* |
| C8 | 0.5442 (2) | 0.5994 (2) | 0.28307 (6) | 0.0417 (4) |
| H8 | 0.631 (2) | 0.552 (3) | 0.2629 (7) | 0.052 (5)* |
| C9 | 0.57317 (17) | 0.6281 (2) | 0.33724 (6) | 0.0332 (3) |
| H9 | 0.680 (2) | 0.607 (2) | 0.3542 (6) | 0.037 (4)* |
| C10 | 0.77427 (16) | 0.7937 (2) | 0.52661 (6) | 0.0338 (3) |
| H10A | 0.769 (2) | 0.910 (3) | 0.5479 (7) | 0.045 (5)* |
| H10B | 0.795 (2) | 0.693 (3) | 0.5525 (8) | 0.054 (5)* |
| H10C | 0.862 (2) | 0.799 (3) | 0.5015 (8) | 0.049 (5)* |
| C11 | 0.50207 (16) | 0.8055 (2) | 0.60909 (5) | 0.0294 (3) |
| H11A | 0.450 (2) | 0.766 (3) | 0.6404 (8) | 0.056 (5)* |
| H11B | 0.601 (2) | 0.738 (3) | 0.6094 (8) | 0.054 (5)* |
| H11C | 0.527 (2) | 0.938 (3) | 0.6128 (8) | 0.063 (6)* |
| C12 | 0.40601 (15) | 0.76834 (17) | 0.55887 (5) | 0.0242 (3) |
| C13 | 0.16041 (15) | 0.78645 (19) | 0.60397 (5) | 0.0266 (3) |
| C14 | 0.05963 (14) | 0.64562 (19) | 0.61874 (5) | 0.0284 (3) |
| C15 | −0.04064 (16) | 0.6879 (2) | 0.65830 (6) | 0.0341 (3) |
| H15 | −0.113 (2) | 0.588 (3) | 0.6692 (7) | 0.045 (5)* |

| | | | | |
|---|---|---|---|---|
| C16 | −0.04014 (16) | 0.8615 (2) | 0.68174 (6) | 0.0366 (3) |
| H16 | −0.112 (2) | 0.889 (3) | 0.7101 (7) | 0.046 (5)* |
| C17 | 0.06066 (17) | 0.9995 (2) | 0.66678 (6) | 0.0367 (3) |
| H17 | 0.062 (2) | 1.130 (3) | 0.6819 (7) | 0.050 (5)* |
| C18 | 0.15980 (16) | 0.9615 (2) | 0.62736 (5) | 0.0325 (3) |
| H18 | 0.2297 (18) | 1.060 (2) | 0.6150 (6) | 0.037 (4)* |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| O1 | 0.0219 (4) | 0.0418 (6) | 0.0276 (5) | −0.0053 (4) | 0.0004 (3) | −0.0017 (4) |
| N1 | 0.0222 (5) | 0.0283 (6) | 0.0236 (5) | −0.0018 (4) | 0.0002 (4) | 0.0002 (4) |
| N2 | 0.0223 (5) | 0.0285 (6) | 0.0301 (6) | −0.0015 (4) | 0.0006 (4) | 0.0002 (5) |
| N3 | 0.0266 (6) | 0.0329 (6) | 0.0232 (5) | −0.0051 (5) | 0.0022 (4) | −0.0021 (5) |
| C1 | 0.0243 (6) | 0.0210 (6) | 0.0289 (6) | −0.0004 (5) | −0.0003 (5) | 0.0008 (5) |
| C2 | 0.0244 (6) | 0.0215 (6) | 0.0243 (6) | −0.0010 (5) | −0.0002 (5) | 0.0003 (5) |
| C3 | 0.0244 (6) | 0.0226 (6) | 0.0253 (6) | −0.0015 (5) | 0.0016 (5) | 0.0010 (5) |
| C4 | 0.0325 (7) | 0.0213 (6) | 0.0235 (6) | −0.0048 (5) | 0.0025 (5) | 0.0009 (5) |
| N4 | 0.0266 (6) | 0.0327 (7) | 0.0626 (9) | −0.0049 (5) | 0.0061 (6) | −0.0072 (6) |
| C5 | 0.0326 (7) | 0.0354 (8) | 0.0267 (6) | −0.0071 (6) | 0.0006 (5) | 0.0046 (6) |
| C6 | 0.0432 (8) | 0.0506 (9) | 0.0274 (7) | −0.0149 (7) | −0.0036 (6) | 0.0073 (7) |
| C7 | 0.0627 (10) | 0.0494 (10) | 0.0233 (7) | −0.0182 (8) | 0.0034 (7) | 0.0001 (7) |
| C8 | 0.0562 (10) | 0.0385 (9) | 0.0321 (7) | −0.0047 (7) | 0.0146 (7) | −0.0037 (7) |
| C9 | 0.0386 (8) | 0.0292 (7) | 0.0323 (7) | 0.0000 (6) | 0.0067 (6) | −0.0004 (6) |
| C10 | 0.0249 (7) | 0.0394 (8) | 0.0363 (7) | −0.0009 (6) | −0.0041 (6) | −0.0039 (7) |
| C11 | 0.0323 (7) | 0.0300 (7) | 0.0254 (6) | −0.0018 (6) | −0.0021 (5) | −0.0013 (6) |
| C12 | 0.0275 (6) | 0.0193 (6) | 0.0257 (6) | −0.0019 (5) | 0.0010 (5) | 0.0017 (5) |
| C13 | 0.0243 (6) | 0.0328 (7) | 0.0229 (6) | −0.0019 (5) | 0.0014 (5) | 0.0021 (5) |
| C14 | 0.0218 (6) | 0.0303 (7) | 0.0324 (7) | −0.0008 (5) | −0.0032 (5) | 0.0045 (6) |
| C15 | 0.0246 (6) | 0.0406 (8) | 0.0375 (7) | −0.0016 (6) | 0.0038 (5) | 0.0093 (6) |
| C16 | 0.0305 (7) | 0.0493 (9) | 0.0309 (7) | 0.0033 (6) | 0.0075 (6) | 0.0031 (7) |
| C17 | 0.0374 (8) | 0.0386 (8) | 0.0345 (7) | 0.0002 (6) | 0.0060 (6) | −0.0040 (7) |
| C18 | 0.0337 (7) | 0.0328 (7) | 0.0316 (7) | −0.0057 (6) | 0.0061 (6) | −0.0009 (6) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| O1—C3 | 1.2554 (15) | C7—H7 | 0.985 (19) |
| N1—C3 | 1.3769 (16) | C8—C9 | 1.392 (2) |
| N1—N2 | 1.3990 (15) | C8—H8 | 0.999 (19) |
| N1—C4 | 1.4178 (16) | C9—H9 | 1.008 (17) |
| N2—C1 | 1.3132 (17) | C10—H10A | 0.99 (2) |
| N3—C12 | 1.3316 (17) | C10—H10B | 0.98 (2) |
| N3—C13 | 1.4330 (16) | C10—H10C | 1.021 (19) |
| N3—H3 | 0.955 (18) | C11—C12 | 1.4962 (18) |
| C1—C2 | 1.4342 (17) | C11—H11A | 0.98 (2) |
| C1—C10 | 1.4906 (18) | C11—H11B | 0.99 (2) |
| C2—C12 | 1.4007 (17) | C11—H11C | 0.98 (2) |
| C2—C3 | 1.4413 (17) | C13—C18 | 1.388 (2) |

| | | | |
|---|---|---|---|
| C4—C5 | 1.3878 (19) | C13—C14 | 1.4017 (18) |
| C4—C9 | 1.3945 (19) | C14—C15 | 1.4007 (19) |
| N4—C14 | 1.3768 (19) | C15—C16 | 1.380 (2) |
| N4—H4A | 0.92 (2) | C15—H15 | 1.000 (18) |
| N4—H4B | 0.93 (2) | C16—C17 | 1.389 (2) |
| C5—C6 | 1.390 (2) | C16—H16 | 1.002 (18) |
| C5—H5 | 0.991 (17) | C17—C18 | 1.385 (2) |
| C6—C7 | 1.385 (2) | C17—H17 | 1.01 (2) |
| C6—H6 | 0.976 (19) | C18—H18 | 0.997 (17) |
| C7—C8 | 1.380 (2) | | |

| | | | |
|---|---|---|---|
| C3—N1—N2 | 111.94 (10) | C8—C9—H9 | 119.9 (9) |
| C3—N1—C4 | 129.21 (11) | C4—C9—H9 | 121.1 (9) |
| N2—N1—C4 | 118.84 (10) | C1—C10—H10A | 111.7 (10) |
| C1—N2—N1 | 106.51 (10) | C1—C10—H10B | 110.7 (12) |
| C12—N3—C13 | 127.72 (11) | H10A—C10—H10B | 105.5 (15) |
| C12—N3—H3 | 112.9 (11) | C1—C10—H10C | 108.2 (11) |
| C13—N3—H3 | 119.2 (11) | H10A—C10—H10C | 111.5 (14) |
| N2—C1—C2 | 111.37 (11) | H10B—C10—H10C | 109.2 (15) |
| N2—C1—C10 | 117.88 (12) | C12—C11—H11A | 112.0 (12) |
| C2—C1—C10 | 130.74 (12) | C12—C11—H11B | 110.7 (11) |
| C12—C2—C1 | 132.12 (12) | H11A—C11—H11B | 107.4 (16) |
| C12—C2—C3 | 122.50 (11) | C12—C11—H11C | 111.3 (12) |
| C1—C2—C3 | 105.35 (11) | H11A—C11—H11C | 108.4 (16) |
| O1—C3—N1 | 126.09 (11) | H11B—C11—H11C | 106.8 (16) |
| O1—C3—C2 | 129.10 (11) | N3—C12—C2 | 117.79 (11) |
| N1—C3—C2 | 104.81 (10) | N3—C12—C11 | 119.49 (11) |
| C5—C4—C9 | 120.57 (13) | C2—C12—C11 | 122.72 (12) |
| C5—C4—N1 | 120.36 (12) | C18—C13—C14 | 121.23 (12) |
| C9—C4—N1 | 119.06 (12) | C18—C13—N3 | 120.55 (12) |
| C14—N4—H4A | 118.0 (13) | C14—C13—N3 | 117.93 (12) |
| C14—N4—H4B | 120.0 (12) | N4—C14—C15 | 120.93 (13) |
| H4A—N4—H4B | 115.7 (17) | N4—C14—C13 | 121.64 (13) |
| C4—C5—C6 | 119.22 (14) | C15—C14—C13 | 117.42 (13) |
| C4—C5—H5 | 121.8 (10) | C16—C15—C14 | 121.21 (13) |
| C6—C5—H5 | 118.9 (10) | C16—C15—H15 | 120.8 (10) |
| C7—C6—C5 | 120.70 (15) | C14—C15—H15 | 118.0 (10) |
| C7—C6—H6 | 120.2 (11) | C15—C16—C17 | 120.71 (13) |
| C5—C6—H6 | 119.1 (11) | C15—C16—H16 | 120.0 (11) |
| C8—C7—C6 | 119.64 (14) | C17—C16—H16 | 119.3 (11) |
| C8—C7—H7 | 119.9 (11) | C18—C17—C16 | 119.10 (14) |
| C6—C7—H7 | 120.5 (11) | C18—C17—H17 | 117.6 (10) |
| C7—C8—C9 | 120.70 (14) | C16—C17—H17 | 123.2 (10) |
| C7—C8—H8 | 121.8 (11) | C17—C18—C13 | 120.32 (13) |
| C9—C8—H8 | 117.5 (11) | C17—C18—H18 | 120.3 (9) |
| C8—C9—C4 | 119.05 (14) | C13—C18—H18 | 119.4 (9) |

| | | | |
|---|---|---|---|
| C3—N1—N2—C1 | −1.13 (14) | C6—C7—C8—C9 | 2.4 (3) |

| | | | |
|---|---|---|---|
| C4—N1—N2—C1 | 178.18 (11) | C7—C8—C9—C4 | 0.1 (2) |
| N1—N2—C1—C2 | 0.78 (14) | C5—C4—C9—C8 | −3.0 (2) |
| N1—N2—C1—C10 | −178.48 (12) | N1—C4—C9—C8 | 177.95 (13) |
| N2—C1—C2—C12 | −178.39 (13) | C13—N3—C12—C2 | −172.18 (12) |
| C10—C1—C2—C12 | 0.7 (2) | C13—N3—C12—C11 | 8.6 (2) |
| N2—C1—C2—C3 | −0.19 (14) | C1—C2—C12—N3 | 179.71 (13) |
| C10—C1—C2—C3 | 178.94 (14) | C3—C2—C12—N3 | 1.77 (18) |
| N2—N1—C3—O1 | −178.75 (12) | C1—C2—C12—C11 | −1.1 (2) |
| C4—N1—C3—O1 | 2.0 (2) | C3—C2—C12—C11 | −179.04 (12) |
| N2—N1—C3—C2 | 0.99 (14) | C12—N3—C13—C18 | 58.78 (19) |
| C4—N1—C3—C2 | −178.23 (12) | C12—N3—C13—C14 | −127.44 (14) |
| C12—C2—C3—O1 | −2.3 (2) | C18—C13—C14—N4 | −179.68 (13) |
| C1—C2—C3—O1 | 179.25 (13) | N3—C13—C14—N4 | 6.59 (19) |
| C12—C2—C3—N1 | 177.93 (11) | C18—C13—C14—C15 | −0.54 (19) |
| C1—C2—C3—N1 | −0.48 (13) | N3—C13—C14—C15 | −174.28 (12) |
| C3—N1—C4—C5 | 21.3 (2) | N4—C14—C15—C16 | 179.20 (13) |
| N2—N1—C4—C5 | −157.89 (12) | C13—C14—C15—C16 | 0.1 (2) |
| C3—N1—C4—C9 | −159.63 (13) | C14—C15—C16—C17 | −0.2 (2) |
| N2—N1—C4—C9 | 21.19 (17) | C15—C16—C17—C18 | 0.8 (2) |
| C9—C4—C5—C6 | 3.4 (2) | C16—C17—C18—C13 | −1.3 (2) |
| N1—C4—C5—C6 | −177.52 (13) | C14—C13—C18—C17 | 1.2 (2) |
| C4—C5—C6—C7 | −1.0 (2) | N3—C13—C18—C17 | 174.77 (13) |
| C5—C6—C7—C8 | −1.9 (3) | | |

*Hydrogen-bond geometry (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N3—H3···O1 | 0.955 (18) | 1.863 (18) | 2.6965 (14) | 144.3 (15) |
| N4—H4*A*···N2$^{i}$ | 0.92 (2) | 2.47 (2) | 3.2542 (17) | 144.1 (16) |
| N4—H4*B*···O1$^{ii}$ | 0.93 (2) | 2.14 (2) | 3.0090 (16) | 153.3 (17) |
| C9—H9···N4$^{i}$ | 1.008 (17) | 2.567 (17) | 3.571 (2) | 173.7 (13) |
| C11—H11*C*···N1$^{iii}$ | 0.98 (2) | 2.68 (2) | 3.5669 (19) | 152.0 (16) |
| C18—H18···N2$^{iii}$ | 0.997 (17) | 2.439 (17) | 3.3984 (18) | 161.2 (13) |

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