# organic compounds

# N′-[6-(3,5-Dimethyl-1H-pyrazol-1-yl)-1,2,4,5-tetrazin-3-yl]butanohydrazide

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In the title compound, $C_{11}H_{16}N_8O$, the tetrazine and pyrazole rings form a dihedral angle of 48.75 (2)°. In the crystal, N—H⋯O and N—H⋯N hydrogen bonds link the molecules into layers parallel to (101).

### Related literature

For related structures, see: Xu et al. (2010, 2011). For applications of 1,2,4,5-tetrazine derivatives, see: Sauer (1996).
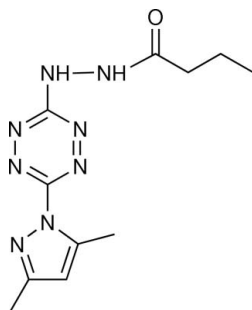


### Experimental

#### Crystal data

| | |
|---|---|
| $C_{11}H_{16}N_8O$ | $a = 10.977$ (3) Å |
| $M_r = 276.32$ | $b = 7.688$ (2) Å |
| Monoclinic, $P2_1/n$ | $c = 15.887$ (5) Å |
| $\beta = 99.798$ (5)° | $\mu = 0.10$ mm$^{-1}$ |
| $V = 1321.2$ (6) Å$^3$ | $T = 103$ K |
| $Z = 4$ | $0.40 \times 0.37 \times 0.33$ mm |
| Mo $K\alpha$ radiation | |

#### Data collection

| | |
|---|---|
| Rigaku AFC10/Saturn724+ diffractometer | 3019 independent reflections |
| 11624 measured reflections | 2570 reflections with $I > 2\sigma(I)$ |
| | $R_{int} = 0.025$ |

#### Refinement

| | |
|---|---|
| $R[F^2 > 2\sigma(F^2)] = 0.036$ | H atoms treated by a mixture of independent and constrained refinement |
| $wR(F^2) = 0.098$ | |
| $S = 1.00$ | |
| 3019 reflections | $\Delta\rho_{max} = 0.30$ e Å$^{-3}$ |
| 192 parameters | $\Delta\rho_{min} = -0.22$ e Å$^{-3}$ |

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

| $D$—H⋯$A$ | $D$—H | H⋯$A$ | $D$⋯$A$ | $D$—H⋯$A$ |
|---|---|---|---|---|
| N14—H14N⋯O17[i] | 0.903 (15) | 1.923 (16) | 2.8221 (15) | 173.8 (14) |
| N15—H15N⋯N8[ii] | 0.880 (16) | 2.008 (16) | 2.8851 (16) | 174.5 (15) |

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

Data collection: *CrystalClear* (Rigaku/MSC, 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: *PLATON* (Spek, 2009); software used to prepare material for publication: *SHELXL97*.

### References

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Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
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Xu, F., Yang, Z. Z., Zhang, S. J. & Hu, W. X. (2011). *Synth. Commun.* **41**, 3367–3375.

# supporting information

## *N*′-[6-(3,5-Dimethyl-1*H*-pyrazol-1-yl)-1,2,4,5-tetrazin-3-yl]butanohydrazide

### Qi-Dong Yan, Feng Xu and Jun Xu

### S1. Comment

1,2,4,5-Tetrazine derivatives exhibit a wide spectrum of antiviral and antitumor properties. They have been used in pesticides and herbicides (Sauer, 1996). In continuation of our search for the structure-activity relationships of 1,2,4,5-tetrazine derivatives (Xu *et al.*, 2010; 2011), we present here the title compound (I).

   In (I) (Fig.1), the tetrazine and pyrazole rings form a dihedral angle of 48.75 (2)°. The N14/N15/C16/O17 and C16/C18/C19 planes make the dihedral angles of 82.56 (2)° and 83.83 (2)°, respectively, with the tetrazine ring. Intermolecular N—H—N and N—H—O hydrogen bonds (Table 1) link molecules into layers parallel to (101) plane (Fig. 2).

### S2. Experimental

3,6-Bis(3,5-dimethyl-1*H*-pyrazol-1-yl)-1,2,4,5-tetrazine (3.0 mmol), chloroform (10 ml) and pyridine(0.25 ml,3.1 mmol) were mixed. Butyryl chloride(3.0 mmol) in chloroform (10 ml) was added dropwise with stirring at room temperature. After the starting 1,2,4,5-tetrazine was completely consumed (the reaction courses was monitored by TLC, ethyl acetate system), evaporation of the chloroform, crude product was obtained and purified by preparative thin-layer chromatography over silica gel GF254(2 mm) (dichloromethane: petroleum ether=1:1). The solution of the compound in anhydrous ethanol was concentrated gradually at room temperature to afford single crystals, which was suitable for X-ray diffraction.

### S3. Refinement

N-bound H atoms were located on a difference map and isotropically refined with N—H bond length restrained to 0.89 (2) Å. Methyl H atoms were placed in calculated positions with C—H = 0.96 Å and torsion angles were refined to fit the electron density, with $U_{iso}(H) = 1.5U_{eq}(C)$. Other C-bound H atoms were placed in calculated positions with C—H = 0.93 Å, and refined in riding mode, with $U_{iso}(H) = 1.2U_{eq}(C)$.
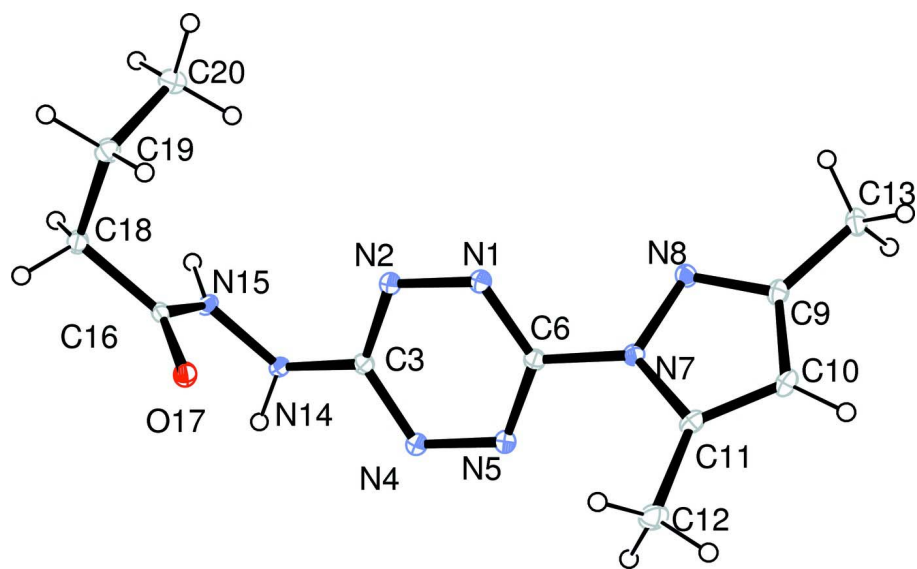
**Figure 1**

The molecular structure of (I) shown with 30% probability displacement ellipsoids.
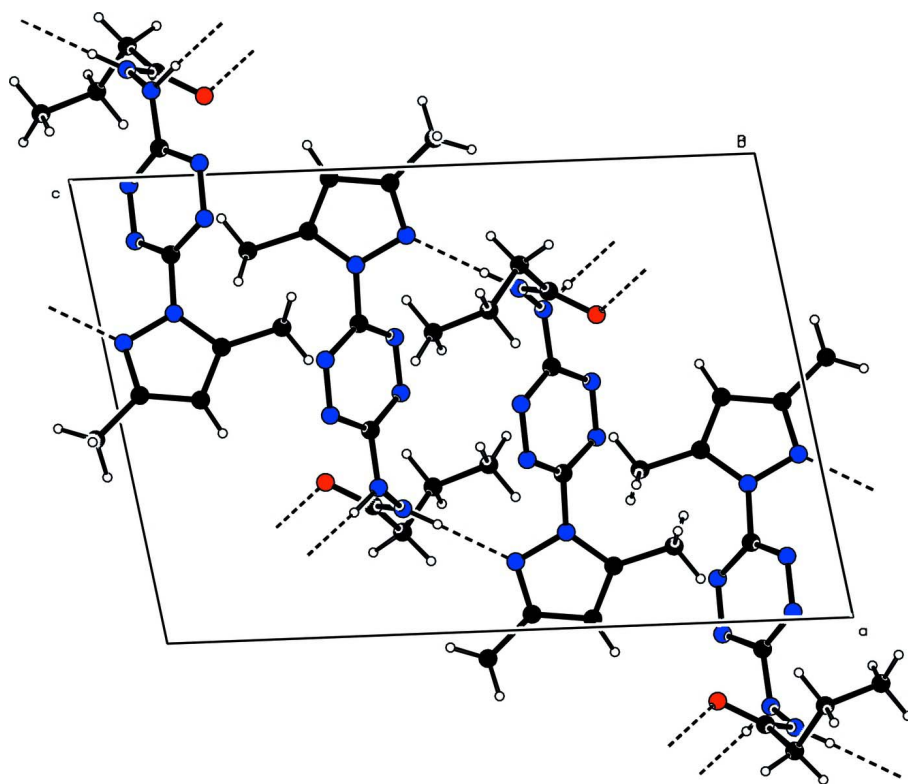


**Figure 2**

A portion of the crystal packing viewed down the *b* axis. N—H⋯O and N—H⋯N hydrogen bonds are shown as dashed lines.

**N′-[6-(3,5-Dimethyl-1H-pyrazol-1-yl)-1,2,4,5-tetrazin-3-yl]butanohydrazide**

*Crystal data*

| | |
|---|---|
| $C_{11}H_{16}N_8O$ | $F(000) = 584$ |
| $M_r = 276.32$ | $D_x = 1.389$ Mg m$^{-3}$ |
| Monoclinic, $P2_1/n$ | Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å |
| Hall symbol: -P 2yn | Cell parameters from 3486 reflections |
| $a = 10.977$ (3) Å | $\theta = 3.3–27.5°$ |
| $b = 7.688$ (2) Å | $\mu = 0.10$ mm$^{-1}$ |
| $c = 15.887$ (5) Å | $T = 103$ K |
| $\beta = 99.798$ (5)° | Block, red |
| $V = 1321.2$ (6) Å$^3$ | $0.40 \times 0.37 \times 0.33$ mm |
| $Z = 4$ | |

*Data collection*

| | |
|---|---|
| Rigaku AFC10/Saturn724+ diffractometer | 3019 independent reflections |
| | 2570 reflections with $I > 2\sigma(I)$ |
| Radiation source: Rotating Anode | $R_{int} = 0.025$ |
| Graphite monochromator | $\theta_{max} = 27.5°$, $\theta_{min} = 3.3°$ |
| Detector resolution: 28.5714 pixels mm$^{-1}$ | $h = -13\rightarrow14$ |
| phi and $\omega$ scans | $k = -9\rightarrow9$ |
| 11624 measured reflections | $l = -20\rightarrow20$ |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | Secondary atom site location: difference Fourier map |
| Least-squares matrix: full | |
| $R[F^2 > 2\sigma(F^2)] = 0.036$ | Hydrogen site location: inferred from neighbouring sites |
| $wR(F^2) = 0.098$ | |
| $S = 1.00$ | H atoms treated by a mixture of independent and constrained refinement |
| 3019 reflections | |
| 192 parameters | $w = 1/[\sigma^2(F_o^2) + (0.0569P)^2 + 0.316P]$ |
| 0 restraints | where $P = (F_o^2 + 2F_c^2)/3$ |
| Primary atom site location: structure-invariant direct methods | $(\Delta/\sigma)_{max} = 0.001$ |
| | $\Delta\rho_{max} = 0.30$ e Å$^{-3}$ |
| | $\Delta\rho_{min} = -0.22$ e Å$^{-3}$ |

*Special details*

**Geometry**. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

**Refinement**. Refinement of $F^2$ against ALL reflections. The weighted $R$-factor $wR$ and goodness of fit $S$ are based on $F^2$, conventional $R$-factors $R$ are based on $F$, with $F$ set to zero for negative $F^2$. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating $R$-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. $R$-factors based on $F^2$ are statistically about twice as large as those based on $F$, and $R$- factors based on ALL data will be even larger.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å$^2$)*

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| O17 | 0.66813 (8) | 0.18530 (11) | 0.72170 (5) | 0.0179 (2) |
| N1 | 0.36379 (9) | 0.45388 (13) | 0.57707 (6) | 0.0166 (2) |
| N2 | 0.48309 (9) | 0.41717 (13) | 0.58523 (6) | 0.0165 (2) |
| N4 | 0.52508 (9) | 0.63680 (13) | 0.69398 (6) | 0.0178 (2) |
| N5 | 0.40619 (9) | 0.67242 (13) | 0.68429 (6) | 0.0178 (2) |

| N7 | 0.20565 (9) | 0.62907 (13) | 0.61117 (6) | 0.0153 (2) |
|---|---|---|---|---|
| N8 | 0.14658 (9) | 0.65755 (13) | 0.52903 (6) | 0.0159 (2) |
| N14 | 0.68389 (9) | 0.49646 (13) | 0.64665 (6) | 0.0149 (2) |
| N15 | 0.73094 (9) | 0.34414 (13) | 0.61788 (6) | 0.0150 (2) |
| C3 | 0.56031 (11) | 0.51505 (15) | 0.64082 (7) | 0.0142 (2) |
| C6 | 0.33149 (11) | 0.58299 (15) | 0.62452 (7) | 0.0147 (2) |
| C9 | 0.03300 (11) | 0.70598 (15) | 0.53650 (8) | 0.0167 (2) |
| C10 | 0.01821 (11) | 0.70610 (16) | 0.62297 (8) | 0.0195 (3) |
| H10 | −0.0548 | 0.7345 | 0.6447 | 0.023* |
| C11 | 0.12946 (11) | 0.65738 (15) | 0.66942 (8) | 0.0175 (3) |
| C12 | 0.16684 (13) | 0.62803 (19) | 0.76288 (8) | 0.0249 (3) |
| H12A | 0.0950 | 0.6437 | 0.7913 | 0.030* |
| H12B | 0.2313 | 0.7116 | 0.7860 | 0.030* |
| H12C | 0.1988 | 0.5094 | 0.7729 | 0.030* |
| C13 | −0.05815 (11) | 0.75347 (17) | 0.45905 (8) | 0.0205 (3) |
| H13A | −0.0631 | 0.8804 | 0.4538 | 0.025* |
| H13B | −0.1396 | 0.7069 | 0.4643 | 0.025* |
| H13C | −0.0316 | 0.7043 | 0.4082 | 0.025* |
| C16 | 0.72224 (10) | 0.19424 (15) | 0.65988 (7) | 0.0146 (2) |
| C18 | 0.78094 (11) | 0.03842 (15) | 0.62567 (7) | 0.0170 (3) |
| H18A | 0.8220 | −0.0332 | 0.6741 | 0.020* |
| H18B | 0.8451 | 0.0783 | 0.5932 | 0.020* |
| C19 | 0.68652 (12) | −0.07353 (16) | 0.56757 (8) | 0.0192 (3) |
| H19A | 0.7237 | −0.1886 | 0.5601 | 0.023* |
| H19B | 0.6138 | −0.0922 | 0.5957 | 0.023* |
| C20 | 0.64377 (12) | 0.00742 (17) | 0.48013 (8) | 0.0217 (3) |
| H20A | 0.6048 | 0.1201 | 0.4869 | 0.026* |
| H20B | 0.5839 | −0.0699 | 0.4458 | 0.026* |
| H20C | 0.7151 | 0.0242 | 0.4513 | 0.026* |
| H14N | 0.7349 (14) | 0.550 (2) | 0.6894 (10) | 0.028 (4)* |
| H15N | 0.7670 (15) | 0.351 (2) | 0.5726 (10) | 0.028 (4)* |

*Atomic displacement parameters (Å$^2$)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| O17 | 0.0175 (4) | 0.0219 (4) | 0.0153 (4) | 0.0035 (3) | 0.0055 (3) | 0.0029 (3) |
| N1 | 0.0149 (5) | 0.0183 (5) | 0.0168 (5) | 0.0010 (4) | 0.0032 (4) | −0.0008 (4) |
| N2 | 0.0146 (5) | 0.0180 (5) | 0.0169 (5) | 0.0016 (4) | 0.0023 (4) | −0.0015 (4) |
| N4 | 0.0161 (5) | 0.0196 (5) | 0.0175 (5) | 0.0025 (4) | 0.0019 (4) | −0.0026 (4) |
| N5 | 0.0160 (5) | 0.0198 (5) | 0.0174 (5) | 0.0027 (4) | 0.0021 (4) | −0.0013 (4) |
| N7 | 0.0152 (5) | 0.0187 (5) | 0.0125 (5) | 0.0019 (4) | 0.0037 (4) | 0.0006 (4) |
| N8 | 0.0146 (5) | 0.0191 (5) | 0.0141 (5) | 0.0013 (4) | 0.0025 (4) | 0.0015 (4) |
| N14 | 0.0146 (5) | 0.0152 (5) | 0.0150 (5) | 0.0011 (4) | 0.0024 (4) | −0.0027 (4) |
| N15 | 0.0163 (5) | 0.0157 (5) | 0.0142 (5) | 0.0021 (4) | 0.0058 (4) | −0.0011 (4) |
| C3 | 0.0168 (6) | 0.0138 (5) | 0.0121 (5) | 0.0009 (4) | 0.0029 (4) | 0.0028 (4) |
| C6 | 0.0158 (5) | 0.0153 (6) | 0.0133 (5) | 0.0009 (4) | 0.0034 (4) | 0.0019 (4) |
| C9 | 0.0142 (5) | 0.0149 (6) | 0.0216 (6) | 0.0001 (4) | 0.0048 (5) | 0.0000 (4) |
| C10 | 0.0178 (6) | 0.0200 (6) | 0.0228 (6) | 0.0028 (5) | 0.0092 (5) | −0.0002 (5) |

| C11 | 0.0200 (6) | 0.0166 (6) | 0.0180 (6) | 0.0006 (5) | 0.0088 (5) | −0.0009 (5) |
| C12 | 0.0294 (7) | 0.0297 (7) | 0.0175 (6) | 0.0039 (6) | 0.0096 (5) | 0.0015 (5) |
| C13 | 0.0145 (6) | 0.0218 (6) | 0.0246 (6) | 0.0018 (5) | 0.0017 (5) | 0.0007 (5) |
| C16 | 0.0113 (5) | 0.0186 (6) | 0.0131 (5) | 0.0012 (4) | −0.0001 (4) | 0.0005 (4) |
| C18 | 0.0168 (6) | 0.0182 (6) | 0.0163 (5) | 0.0036 (5) | 0.0037 (4) | 0.0012 (5) |
| C19 | 0.0216 (6) | 0.0164 (6) | 0.0199 (6) | 0.0004 (5) | 0.0048 (5) | 0.0000 (5) |
| C20 | 0.0216 (6) | 0.0240 (7) | 0.0189 (6) | −0.0028 (5) | 0.0023 (5) | −0.0015 (5) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| O17—C16 | 1.2332 (14) | C10—H10 | 0.9500 |
| N1—N2 | 1.3243 (14) | C11—C12 | 1.4887 (17) |
| N1—C6 | 1.3304 (15) | C12—H12A | 0.9800 |
| N2—C3 | 1.3453 (16) | C12—H12B | 0.9800 |
| N4—N5 | 1.3166 (14) | C12—H12C | 0.9800 |
| N4—C3 | 1.3602 (15) | C13—H13A | 0.9800 |
| N5—C6 | 1.3349 (15) | C13—H13B | 0.9800 |
| N7—C11 | 1.3663 (15) | C13—H13C | 0.9800 |
| N7—N8 | 1.3723 (13) | C16—C18 | 1.5049 (16) |
| N7—C6 | 1.4068 (15) | C18—C19 | 1.5301 (17) |
| N8—C9 | 1.3258 (15) | C18—H18A | 0.9900 |
| N14—C3 | 1.3515 (15) | C18—H18B | 0.9900 |
| N14—N15 | 1.3883 (14) | C19—C20 | 1.5216 (17) |
| N14—H14N | 0.904 (16) | C19—H19A | 0.9900 |
| N15—C16 | 1.3432 (15) | C19—H19B | 0.9900 |
| N15—H15N | 0.880 (17) | C20—H20A | 0.9800 |
| C9—C10 | 1.4104 (17) | C20—H20B | 0.9800 |
| C9—C13 | 1.4932 (17) | C20—H20C | 0.9800 |
| C10—C11 | 1.3674 (17) | | |
| | | | |
| N2—N1—C6 | 117.26 (10) | H12A—C12—H12B | 109.5 |
| N1—N2—C3 | 116.57 (10) | C11—C12—H12C | 109.5 |
| N5—N4—C3 | 116.84 (10) | H12A—C12—H12C | 109.5 |
| N4—N5—C6 | 116.92 (10) | H12B—C12—H12C | 109.5 |
| C11—N7—N8 | 111.97 (10) | C9—C13—H13A | 109.5 |
| C11—N7—C6 | 129.54 (10) | C9—C13—H13B | 109.5 |
| N8—N7—C6 | 118.45 (9) | H13A—C13—H13B | 109.5 |
| C9—N8—N7 | 105.01 (9) | C9—C13—H13C | 109.5 |
| C3—N14—N15 | 119.47 (10) | H13A—C13—H13C | 109.5 |
| C3—N14—H14N | 119.3 (10) | H13B—C13—H13C | 109.5 |
| N15—N14—H14N | 114.6 (10) | O17—C16—N15 | 121.87 (11) |
| C16—N15—N14 | 119.89 (10) | O17—C16—C18 | 122.49 (11) |
| C16—N15—H15N | 122.5 (10) | N15—C16—C18 | 115.63 (10) |
| N14—N15—H15N | 117.6 (10) | C16—C18—C19 | 112.20 (10) |
| N2—C3—N14 | 119.92 (10) | C16—C18—H18A | 109.2 |
| N2—C3—N4 | 125.35 (11) | C19—C18—H18A | 109.2 |
| N14—C3—N4 | 114.73 (10) | C16—C18—H18B | 109.2 |
| N1—C6—N5 | 126.63 (11) | C19—C18—H18B | 109.2 |

| | | | |
|---|---|---|---|
| N1—C6—N7 | 116.88 (10) | H18A—C18—H18B | 107.9 |
| N5—C6—N7 | 116.49 (10) | C20—C19—C18 | 113.12 (10) |
| N8—C9—C10 | 110.69 (11) | C20—C19—H19A | 109.0 |
| N8—C9—C13 | 120.23 (10) | C18—C19—H19A | 109.0 |
| C10—C9—C13 | 129.07 (11) | C20—C19—H19B | 109.0 |
| C11—C10—C9 | 106.57 (11) | C18—C19—H19B | 109.0 |
| C11—C10—H10 | 126.7 | H19A—C19—H19B | 107.8 |
| C9—C10—H10 | 126.7 | C19—C20—H20A | 109.5 |
| N7—C11—C10 | 105.75 (10) | C19—C20—H20B | 109.5 |
| N7—C11—C12 | 123.70 (11) | H20A—C20—H20B | 109.5 |
| C10—C11—C12 | 130.47 (11) | C19—C20—H20C | 109.5 |
| C11—C12—H12A | 109.5 | H20A—C20—H20C | 109.5 |
| C11—C12—H12B | 109.5 | H20B—C20—H20C | 109.5 |
| | | | |
| C6—N1—N2—C3 | −0.22 (15) | C11—N7—C6—N5 | −46.50 (17) |
| C3—N4—N5—C6 | 1.40 (16) | N8—N7—C6—N5 | 130.92 (11) |
| C11—N7—N8—C9 | 0.71 (13) | N7—N8—C9—C10 | −0.93 (13) |
| C6—N7—N8—C9 | −177.14 (10) | N7—N8—C9—C13 | 178.23 (10) |
| C3—N14—N15—C16 | −68.57 (14) | N8—C9—C10—C11 | 0.84 (14) |
| N1—N2—C3—N14 | −173.71 (10) | C13—C9—C10—C11 | −178.22 (12) |
| N1—N2—C3—N4 | 6.04 (17) | N8—N7—C11—C10 | −0.20 (14) |
| N15—N14—C3—N2 | −20.85 (16) | C6—N7—C11—C10 | 177.35 (11) |
| N15—N14—C3—N4 | 159.37 (10) | N8—N7—C11—C12 | 176.86 (11) |
| N5—N4—C3—N2 | −6.68 (17) | C6—N7—C11—C12 | −5.59 (19) |
| N5—N4—C3—N14 | 173.08 (10) | C9—C10—C11—N7 | −0.36 (13) |
| N2—N1—C6—N5 | −5.02 (18) | C9—C10—C11—C12 | −177.15 (13) |
| N2—N1—C6—N7 | 175.72 (10) | N14—N15—C16—O17 | 3.44 (17) |
| N4—N5—C6—N1 | 4.37 (18) | N14—N15—C16—C18 | −177.48 (9) |
| N4—N5—C6—N7 | −176.37 (10) | O17—C16—C18—C19 | 80.97 (14) |
| C11—N7—C6—N1 | 132.83 (12) | N15—C16—C18—C19 | −98.10 (12) |
| N8—N7—C6—N1 | −49.75 (15) | C16—C18—C19—C20 | 74.42 (13) |

*Hydrogen-bond geometry (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N14—H14*N*···O17ⁱ | 0.903 (15) | 1.923 (16) | 2.8221 (15) | 173.8 (14) |
| N15—H15*N*···N8ⁱⁱ | 0.880 (16) | 2.008 (16) | 2.8851 (16) | 174.5 (15) |

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