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# $N^1$,$N^4$,3,6-Tetramethyl-1,2,4,5-tetrazine-1,4-dicarboxamide

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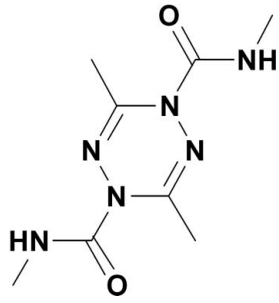
Key indicators: single-crystal X-ray study; $T$ = 298 K; mean $\sigma$(C–C) = 0.003 Å; $R$ factor = 0.044; $wR$ factor = 0.115; data-to-parameter ratio = 12.8.

The asymmetric unit of the title compound, $C_8H_{14}N_6O_2$, contains two independent molecules. In one molecule, the amide-substituted N atoms of the tetrazine ring deviate from the plane [maximum deviation = 0.028 (1) Å] through the four other atoms in the ring by 0.350 (2) and 0.344 (2) Å, forming a boat conformation, and the mean planes of the two carboxamide groups form dihedral angles of 10.46 (13) and 20.41 (12)° with the four approximtely planar atoms in the tetrazine ring. In the other molecule, the amide-substituted N atoms of the tetrazine ring deviate from the plane [maximum deviation = 0.033 (1) Å] through the four other atoms in the ring by 0.324 (2) and 0.307 (2) Å, forming a boat conformation, and the mean planes of the two carboxamide groups form dihedral angles of 14.66 (11) and 17.08 (10)° with the four approximately planar atoms of the tetrazine ring. In the crystal, N—H···O hydrogen bonds connect molecules to form a two-dimensional network parallel to ($1\bar{1}\bar{1}$). Intramolecular N—H···N hydrogen bonds are observed.

## Related literature

For chemical reactions of 1,2,4,5-tetrazine derivatives, see: Domingo *et al.* (2009); Lorincz *et al.* (2010) and for their biological activity, see: Devaraj *et al.* (2009); Eremeev *et al.* (1978, 1980); Han *et al.* (2010); Neunhoeffer (1984); Sauer (1996). For the antitumor activity of 1,2,4,5-tetrazine derivatives, see: Hu *et al.* (2002, 2004); Rao & Hu (2005, 2006). For standard bond lengths, see: Allen *et al.* (1987). For the synthesis of the title compound, see: Hu *et al.* (2004); Rao *et al.* (2012); Sun *et al.* (2003).



## Experimental

### Crystal data

$C_8H_{14}N_6O_2$
$M_r$ = 226.25
Triclinic, $P\bar{1}$
$a$ = 9.0002 (17) Å
$b$ = 12.045 (2) Å
$c$ = 12.357 (2) Å
$\alpha$ = 118.386 (2)°
$\beta$ = 101.701 (3)°
$\gamma$ = 99.494 (3)°
$V$ = 1099.6 (4) Å$^3$
$Z$ = 4
Mo $K\alpha$ radiation
$\mu$ = 0.10 mm$^{-1}$
$T$ = 298 K
0.34 × 0.30 × 0.15 mm

### Data collection

Bruker SMART CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 1997)
$T_{min}$ = 0.966, $T_{max}$ = 0.985
5571 measured reflections
3809 independent reflections
3178 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.018

### Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.044
$wR(F^2)$ = 0.115
$S$ = 1.06
3809 reflections
298 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.17 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.19 e Å$^{-3}$

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| N3—H3···N2 | 0.86 | 2.16 | 2.572 (2) | 108 |
| N6—H6···N5 | 0.86 | 2.19 | 2.586 (2) | 108 |
| N9—H9···N8 | 0.86 | 2.15 | 2.567 (2) | 109 |
| N12—H12···N11 | 0.86 | 2.17 | 2.581 (2) | 109 |
| N3—H3···O4 | 0.86 | 2.20 | 2.925 (2) | 142 |
| N6—H6···O3$^{i}$ | 0.86 | 2.16 | 2.918 (2) | 146 |
| N9—H9···O1$^{ii}$ | 0.86 | 2.14 | 2.877 (3) | 143 |
| N12—H12···O2$^{iii}$ | 0.86 | 2.24 | 2.967 (3) | 142 |

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

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINT* (Bruker, 1997); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *PLATON* (Spek, 2009); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: LH5475).

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# supporting information

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## $N^1$,$N^4$,3,6-Tetramethyl-1,2,4,5-tetrazine-1,4-dicarboxamide

**Na-Bo Sun, Guo-Wu Rao and Qun Shen**

### S1. Comment

Tetrazine derivatives have high activity in chemical reactions (Domingo *et al.*, 2009; Lorincz *et al.*, 2010), and have been widely used in pesticides and medicines (Devaraj *et al.*, 2009; Eremeev *et al.*,1978, 1980; Han *et al.*, 2010; Neunhoeffer, 1984; Sauer, 1996). In a continuation of our studies of antitumor activities in 1,2,4,5-tetrazine derivatives (Hu *et al.*, 2002, 2004; Rao & Hu, 2005, 2006), we have obtained a colourless crystalline compound, (I). The structure was confirmed by single-crystal X-ray diffraction.

The two molecules forming the asymmetric unit of (I) are shown in Fig. 1. The C=N, N—N and C—N bonds have normal distances (Allen *et al.*, 1987). The tetrazine rings are 1,4-dihydro structure with the N-substituted groups at the 1,4-positions.

In (I), atoms N2, C3, N5 and C6 are approximately planar, with the largest deviation from this plane being 0.028 (1) Å. Atoms N1 and N4 deviate from this plane by 0.350 (2) and 0.344 (2) Å, respectively. Atoms N8, C9, N11 and C12 are approximately planar, with the largest deviation from this plane being 0.033 (1) Å. Atoms N7 and N10 deviate from this plane by 0.324 (2) and 0.307 (2) Å, respectively. The dihedral angle between the N2/C3/N5/C6 plane and the N1/N2/C6 plane is 27.99 (16)°, and between the N2/C3/N5/C6 plane and the N4/N5/C3 plane is 27.91 (16)°. The dihedral angle between the N8/C9/N11/C12 plane and the N7/N8/C12 plane is 26.36 (14)°, and between the N8/C9/N11/C12 plane and the N10/N11/C9 plane is 24.96 (13)°. The tetrazine ring exhibits a boat conformation. Atoms O1, C4, N3 and C7 are approximately planar, with the largest deviation from this plane being 0.016 (1) Å. Atoms O2, C5, N6 and C8 are approximately planar, with the largest deviation from this plane being -0.022 (1) Å. Atoms O3, C13, N9 and C15 are approximately planar, with the largest deviation from this plane being 0.004 (1) Å. Atoms O4, C14, N12 and C16 are approximately planar, with the largest deviation from this plane being -0.005 (1) Å. The dihedral angles between the N2/C3/N5/C6 plane and two planes of carboxamide groups are 10.46 (13) and 20.41 (12)°, respectively. The dihedral angles between the N8/C9/N11/C12 plane and two planes of carboxamide groups are 14.66 (11) and 17.08 (10)°, respectively. Intramolecular N—H···N hydrogen bonds are observed. In the crystal, N—H···O hydrogen bonds connect molecules to form a two-dimensional network parallel to $(1\overline{1}\overline{1})$ (Fig. 2).

### S2. Experimental

The title compound was the product of the reaction of 3,6-dimethyl-1,6-dihydro-1,2,4,5-tetrazine, bis(trichloromethyl) carbonate and methanamine according to the procedure (Hu *et al.*, 2004; Rao *et al.*, 2012; Sun *et al.*, 2003). A solution of the compound in ethanol was concentrated gradually at room temperature to afford colourless blocks.

### S3. Refinement

H atoms were included in calculated positions and refined using a riding model. H atoms were given isotropic displacement parameters equal to 1.2 (or 1.5 for methyl H atoms) times the equivalent isotropic displacement parameters

of their parent atoms, and C—H distances were set to 0.96 Å for methyl H atoms, while N—H distances were set to 0.86 Å.

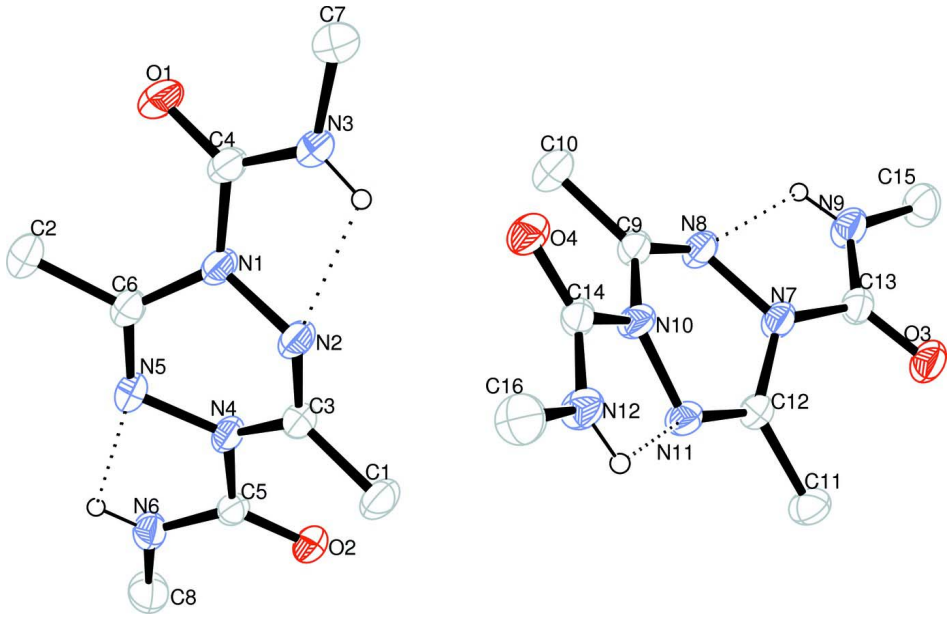


**Figure 1**

The molecular structure of (I), shown with 30% probability displacement ellipsoids. Hydrogen bonds are shown as dashed lines.

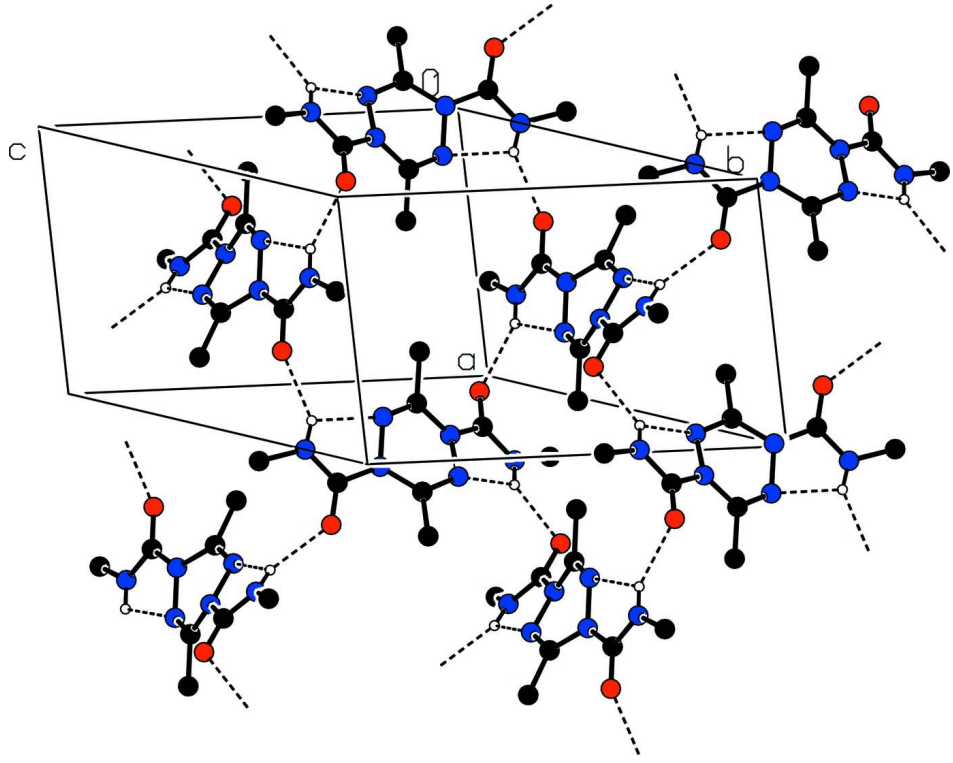

**Figure 2**

Part of the crystal structure with hydrogen donds shown as dashed lines.

### *N*$^1$,*N*$^4$,3,6-Tetramethyl-1,2,4,5-tetrazine-1,4-dicarboxamide

*Crystal data*

$C_8H_{14}N_6O_2$
$M_r = 226.25$
Triclinic, $P\overline{1}$
Hall symbol: -P 1
$a = 9.0002$ (17) Å
$b = 12.045$ (2) Å
$c = 12.357$ (2) Å
$\alpha = 118.386$ (2)°
$\beta = 101.701$ (3)°
$\gamma = 99.494$ (3)°
$V = 1099.6$ (4) Å$^3$
$Z = 4$
$F(000) = 480$
$D_x = 1.367$ Mg m$^{-3}$
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 2161 reflections
$\theta = 2.4$–$26.0°$
$\mu = 0.10$ mm$^{-1}$
$T = 298$ K
Block, colourless
0.34 × 0.30 × 0.15 mm

*Data collection*

Bruker SMART CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
$\varphi$ and $\omega$ scans
Absorption correction: multi-scan (*SADABS*; Bruker, 1997)
$T_{min} = 0.966$, $T_{max} = 0.985$
5571 measured reflections
3809 independent reflections
3178 reflections with $I > 2\sigma(I)$
$R_{int} = 0.018$
$\theta_{max} = 25.0°$, $\theta_{min} = 1.9°$
$h = -10 \rightarrow 10$
$k = -14 \rightarrow 11$
$l = -11 \rightarrow 14$

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.044$
$wR(F^2) = 0.115$
$S = 1.06$
3809 reflections
298 parameters
0 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
$w = 1/[\sigma^2(F_o^2) + (0.0511P)^2 + 0.2386P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.17$ e Å$^{-3}$
$\Delta\rho_{min} = -0.19$ e Å$^{-3}$
Extinction correction: *SHELXL97* (Sheldrick, 2008), $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.028 (2)

*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 (Å²)*

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| O2 | 0.65578 (15) | 1.05745 (12) | 0.47718 (12) | 0.0481 (3) |
| O4 | 0.89425 (15) | 0.52517 (12) | 0.38657 (12) | 0.0485 (3) |
| O3 | 1.24324 (16) | 0.92428 (15) | 1.04950 (13) | 0.0591 (4) |
| O1 | 0.31715 (16) | 0.38004 (14) | 0.09001 (15) | 0.0624 (4) |
| N11 | 1.11229 (17) | 0.83375 (14) | 0.67258 (14) | 0.0413 (4) |
| N5 | 0.42071 (17) | 0.76464 (15) | 0.18158 (14) | 0.0428 (4) |
| N8 | 0.90988 (17) | 0.73177 (15) | 0.76534 (14) | 0.0441 (4) |
| N1 | 0.48121 (17) | 0.59229 (14) | 0.19776 (14) | 0.0427 (4) |
| N4 | 0.54445 (17) | 0.84531 (14) | 0.30278 (14) | 0.0408 (4) |
| N2 | 0.64314 (17) | 0.67031 (15) | 0.26959 (15) | 0.0456 (4) |
| N10 | 0.99591 (17) | 0.70658 (13) | 0.59312 (13) | 0.0401 (4) |
| N7 | 1.06880 (17) | 0.81490 (15) | 0.84255 (14) | 0.0424 (4) |
| C5 | 0.5569 (2) | 0.98150 (17) | 0.36969 (17) | 0.0389 (4) |
| C9 | 0.8816 (2) | 0.67574 (17) | 0.64282 (17) | 0.0389 (4) |
| N12 | 1.10612 (19) | 0.69002 (15) | 0.43553 (14) | 0.0459 (4) |
| H12 | 1.1731 | 0.7660 | 0.4950 | 0.055* |
| C12 | 1.1485 (2) | 0.88147 (16) | 0.79504 (16) | 0.0378 (4) |
| N3 | 0.57057 (19) | 0.42708 (15) | 0.20694 (15) | 0.0479 (4) |
| H3 | 0.6588 | 0.4886 | 0.2591 | 0.058* |
| C4 | 0.4495 (2) | 0.45756 (18) | 0.15889 (17) | 0.0432 (4) |
| N6 | 0.45245 (19) | 1.01525 (15) | 0.30820 (15) | 0.0470 (4) |
| H6 | 0.3919 | 0.9577 | 0.2297 | 0.056* |
| N9 | 0.99787 (19) | 0.79818 (17) | 1.00444 (15) | 0.0511 (4) |
| H9 | 0.9073 | 0.7470 | 0.9458 | 0.061* |
| C14 | 0.9928 (2) | 0.63353 (17) | 0.46360 (16) | 0.0379 (4) |
| C3 | 0.6682 (2) | 0.79506 (18) | 0.32349 (17) | 0.0408 (4) |
| C13 | 1.1104 (2) | 0.85187 (18) | 0.97372 (17) | 0.0425 (4) |
| C6 | 0.3891 (2) | 0.64048 (18) | 0.13459 (17) | 0.0394 (4) |
| C10 | 0.7187 (2) | 0.5826 (2) | 0.55809 (19) | 0.0531 (5) |
| H10A | 0.6737 | 0.6075 | 0.4987 | 0.080* |
| H10B | 0.6527 | 0.5861 | 0.6110 | 0.080* |
| H10C | 0.7249 | 0.4941 | 0.5100 | 0.080* |
| C11 | 1.2743 (2) | 1.01175 (18) | 0.88275 (18) | 0.0505 (5) |
| H11A | 1.2369 | 1.0699 | 0.9493 | 0.076* |
| H11B | 1.2985 | 1.0501 | 0.8334 | 0.076* |
| H11C | 1.3685 | 0.9993 | 0.9221 | 0.076* |
| C1 | 0.8344 (2) | 0.88257 (19) | 0.4028 (2) | 0.0555 (5) |
| H1A | 0.8627 | 0.9432 | 0.3753 | 0.083* |
| H1B | 0.9055 | 0.8296 | 0.3914 | 0.083* |
| H1C | 0.8422 | 0.9314 | 0.4929 | 0.083* |
| C2 | 0.2535 (2) | 0.5519 (2) | 0.01109 (18) | 0.0531 (5) |
| H2A | 0.2876 | 0.4846 | −0.0507 | 0.080* |
| H2B | 0.2182 | 0.6029 | −0.0235 | 0.080* |
| H2C | 0.1676 | 0.5110 | 0.0279 | 0.080* |
| C15 | 1.0255 (3) | 0.8246 (2) | 1.13515 (19) | 0.0585 (6) |

| | | | | |
|---|---|---|---|---|
| H15A | 0.9317 | 0.7778 | 1.1395 | 0.088* |
| H15B | 1.0496 | 0.9179 | 1.1949 | 0.088* |
| H15C | 1.1133 | 0.7955 | 1.1578 | 0.088* |
| C7 | 0.5575 (3) | 0.29262 (19) | 0.1735 (2) | 0.0622 (6) |
| H7A | 0.6410 | 0.2931 | 0.2361 | 0.093* |
| H7B | 0.5669 | 0.2428 | 0.0886 | 0.093* |
| H7C | 0.4561 | 0.2527 | 0.1736 | 0.093* |
| C8 | 0.4394 (3) | 1.1471 (2) | 0.3715 (2) | 0.0615 (6) |
| H8A | 0.3507 | 1.1515 | 0.3172 | 0.092* |
| H8B | 0.5354 | 1.2086 | 0.3867 | 0.092* |
| H8C | 0.4235 | 1.1694 | 0.4530 | 0.092* |
| C16 | 1.1183 (3) | 0.6249 (2) | 0.30563 (19) | 0.0606 (6) |
| H16A | 1.2061 | 0.6797 | 0.3028 | 0.091* |
| H16B | 1.0215 | 0.6108 | 0.2444 | 0.091* |
| H16C | 1.1354 | 0.5413 | 0.2838 | 0.091* |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| O2 | 0.0450 (7) | 0.0421 (7) | 0.0381 (7) | 0.0013 (6) | 0.0023 (6) | 0.0150 (6) |
| O4 | 0.0481 (8) | 0.0373 (7) | 0.0384 (7) | 0.0026 (6) | 0.0046 (6) | 0.0109 (6) |
| O3 | 0.0435 (8) | 0.0760 (10) | 0.0429 (8) | −0.0041 (7) | −0.0020 (6) | 0.0335 (8) |
| O1 | 0.0390 (8) | 0.0510 (8) | 0.0730 (10) | −0.0083 (7) | −0.0028 (7) | 0.0297 (8) |
| N11 | 0.0412 (9) | 0.0335 (8) | 0.0358 (8) | 0.0004 (6) | 0.0062 (7) | 0.0142 (7) |
| N5 | 0.0354 (8) | 0.0437 (9) | 0.0340 (8) | 0.0057 (7) | 0.0019 (7) | 0.0148 (7) |
| N8 | 0.0333 (8) | 0.0458 (9) | 0.0382 (9) | 0.0007 (7) | 0.0040 (7) | 0.0176 (7) |
| N1 | 0.0308 (8) | 0.0387 (8) | 0.0433 (9) | 0.0011 (6) | 0.0026 (7) | 0.0170 (7) |
| N4 | 0.0337 (8) | 0.0375 (8) | 0.0354 (8) | 0.0039 (6) | 0.0007 (6) | 0.0139 (7) |
| N2 | 0.0311 (8) | 0.0403 (9) | 0.0478 (9) | 0.0012 (7) | −0.0003 (7) | 0.0183 (7) |
| N10 | 0.0405 (8) | 0.0330 (8) | 0.0312 (8) | −0.0004 (6) | 0.0054 (6) | 0.0114 (6) |
| N7 | 0.0351 (8) | 0.0463 (9) | 0.0337 (8) | 0.0013 (7) | 0.0041 (6) | 0.0184 (7) |
| C5 | 0.0347 (9) | 0.0410 (10) | 0.0344 (10) | 0.0026 (8) | 0.0086 (8) | 0.0189 (8) |
| C9 | 0.0371 (10) | 0.0357 (9) | 0.0355 (10) | 0.0080 (8) | 0.0059 (8) | 0.0157 (8) |
| N12 | 0.0478 (9) | 0.0414 (8) | 0.0337 (8) | 0.0040 (7) | 0.0104 (7) | 0.0130 (7) |
| C12 | 0.0356 (9) | 0.0359 (9) | 0.0345 (10) | 0.0071 (7) | 0.0074 (8) | 0.0157 (8) |
| N3 | 0.0419 (9) | 0.0375 (8) | 0.0465 (9) | 0.0002 (7) | −0.0005 (7) | 0.0184 (7) |
| C4 | 0.0376 (10) | 0.0399 (10) | 0.0386 (10) | −0.0003 (8) | 0.0084 (8) | 0.0162 (8) |
| N6 | 0.0510 (10) | 0.0433 (9) | 0.0371 (8) | 0.0113 (7) | 0.0055 (7) | 0.0184 (7) |
| N9 | 0.0410 (9) | 0.0636 (11) | 0.0379 (9) | 0.0014 (8) | 0.0068 (7) | 0.0257 (8) |
| C14 | 0.0378 (10) | 0.0345 (9) | 0.0340 (9) | 0.0101 (8) | 0.0042 (8) | 0.0158 (8) |
| C3 | 0.0355 (10) | 0.0417 (10) | 0.0388 (10) | 0.0050 (8) | 0.0065 (8) | 0.0206 (8) |
| C13 | 0.0381 (10) | 0.0469 (11) | 0.0361 (10) | 0.0085 (8) | 0.0051 (8) | 0.0211 (9) |
| C6 | 0.0315 (9) | 0.0438 (10) | 0.0340 (9) | 0.0060 (8) | 0.0092 (7) | 0.0162 (8) |
| C10 | 0.0392 (11) | 0.0532 (12) | 0.0458 (11) | 0.0014 (9) | 0.0072 (9) | 0.0170 (10) |
| C11 | 0.0526 (12) | 0.0416 (10) | 0.0386 (10) | −0.0013 (9) | 0.0072 (9) | 0.0152 (9) |
| C1 | 0.0326 (10) | 0.0471 (11) | 0.0675 (14) | 0.0022 (9) | −0.0023 (9) | 0.0262 (10) |
| C2 | 0.0467 (12) | 0.0517 (12) | 0.0385 (11) | 0.0049 (9) | 0.0006 (9) | 0.0155 (9) |
| C15 | 0.0535 (13) | 0.0769 (15) | 0.0432 (11) | 0.0097 (11) | 0.0124 (10) | 0.0345 (11) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C7 | 0.0627 (14) | 0.0434 (11) | 0.0638 (14) | 0.0043 (10) | 0.0048 (11) | 0.0257 (11) |
| C8 | 0.0726 (15) | 0.0491 (12) | 0.0582 (13) | 0.0209 (11) | 0.0138 (12) | 0.0271 (11) |
| C16 | 0.0711 (15) | 0.0603 (13) | 0.0410 (11) | 0.0120 (11) | 0.0205 (11) | 0.0215 (10) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| O2—C5 | 1.221 (2) | N6—H6 | 0.8600 |
| O4—C14 | 1.221 (2) | N9—C13 | 1.327 (2) |
| O3—C13 | 1.221 (2) | N9—C15 | 1.447 (2) |
| O1—C4 | 1.217 (2) | N9—H9 | 0.8600 |
| N11—C12 | 1.280 (2) | C3—C1 | 1.487 (2) |
| N11—N10 | 1.4251 (19) | C6—C2 | 1.491 (2) |
| N5—C6 | 1.274 (2) | C10—H10A | 0.9600 |
| N5—N4 | 1.418 (2) | C10—H10B | 0.9600 |
| N8—C9 | 1.276 (2) | C10—H10C | 0.9600 |
| N8—N7 | 1.423 (2) | C11—H11A | 0.9600 |
| N1—C6 | 1.400 (2) | C11—H11B | 0.9600 |
| N1—C4 | 1.413 (2) | C11—H11C | 0.9600 |
| N1—N2 | 1.423 (2) | C1—H1A | 0.9600 |
| N4—C3 | 1.388 (2) | C1—H1B | 0.9600 |
| N4—C5 | 1.414 (2) | C1—H1C | 0.9600 |
| N2—C3 | 1.276 (2) | C2—H2A | 0.9600 |
| N10—C9 | 1.386 (2) | C2—H2B | 0.9600 |
| N10—C14 | 1.404 (2) | C2—H2C | 0.9600 |
| N7—C12 | 1.390 (2) | C15—H15A | 0.9600 |
| N7—C13 | 1.406 (2) | C15—H15B | 0.9600 |
| C5—N6 | 1.325 (2) | C15—H15C | 0.9600 |
| C9—C10 | 1.491 (2) | C7—H7A | 0.9600 |
| N12—C14 | 1.328 (2) | C7—H7B | 0.9600 |
| N12—C16 | 1.451 (2) | C7—H7C | 0.9600 |
| N12—H12 | 0.8600 | C8—H8A | 0.9600 |
| C12—C11 | 1.489 (2) | C8—H8B | 0.9600 |
| N3—C4 | 1.323 (2) | C8—H8C | 0.9600 |
| N3—C7 | 1.445 (2) | C16—H16A | 0.9600 |
| N3—H3 | 0.8600 | C16—H16B | 0.9600 |
| N6—C8 | 1.437 (3) | C16—H16C | 0.9600 |

| | | | |
|---|---|---|---|
| C12—N11—N10 | 114.96 (14) | N5—C6—C2 | 117.15 (17) |
| C6—N5—N4 | 115.19 (15) | N1—C6—C2 | 122.75 (16) |
| C9—N8—N7 | 115.02 (15) | C9—C10—H10A | 109.5 |
| C6—N1—C4 | 124.52 (15) | C9—C10—H10B | 109.5 |
| C6—N1—N2 | 116.29 (14) | H10A—C10—H10B | 109.5 |
| C4—N1—N2 | 114.69 (14) | C9—C10—H10C | 109.5 |
| C3—N4—C5 | 124.12 (14) | H10A—C10—H10C | 109.5 |
| C3—N4—N5 | 116.73 (14) | H10B—C10—H10C | 109.5 |
| C5—N4—N5 | 115.63 (14) | C12—C11—H11A | 109.5 |
| C3—N2—N1 | 114.98 (15) | C12—C11—H11B | 109.5 |
| C9—N10—C14 | 125.66 (14) | H11A—C11—H11B | 109.5 |

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|---|---|---|---|
| C9—N10—N11 | 117.72 (13) | C12—C11—H11C | 109.5 |
| C14—N10—N11 | 115.71 (14) | H11A—C11—H11C | 109.5 |
| C12—N7—C13 | 124.70 (15) | H11B—C11—H11C | 109.5 |
| C12—N7—N8 | 117.36 (14) | C3—C1—H1A | 109.5 |
| C13—N7—N8 | 114.98 (14) | C3—C1—H1B | 109.5 |
| O2—C5—N6 | 124.99 (17) | H1A—C1—H1B | 109.5 |
| O2—C5—N4 | 120.13 (16) | C3—C1—H1C | 109.5 |
| N6—C5—N4 | 114.86 (15) | H1A—C1—H1C | 109.5 |
| N8—C9—N10 | 120.67 (16) | H1B—C1—H1C | 109.5 |
| N8—C9—C10 | 116.79 (17) | C6—C2—H2A | 109.5 |
| N10—C9—C10 | 122.46 (16) | C6—C2—H2B | 109.5 |
| C14—N12—C16 | 120.73 (16) | H2A—C2—H2B | 109.5 |
| C14—N12—H12 | 119.6 | C6—C2—H2C | 109.5 |
| C16—N12—H12 | 119.6 | H2A—C2—H2C | 109.5 |
| N11—C12—N7 | 120.50 (15) | H2B—C2—H2C | 109.5 |
| N11—C12—C11 | 117.34 (16) | N9—C15—H15A | 109.5 |
| N7—C12—C11 | 122.13 (15) | N9—C15—H15B | 109.5 |
| C4—N3—C7 | 121.39 (16) | H15A—C15—H15B | 109.5 |
| C4—N3—H3 | 119.3 | N9—C15—H15C | 109.5 |
| C7—N3—H3 | 119.3 | H15A—C15—H15C | 109.5 |
| O1—C4—N3 | 124.76 (18) | H15B—C15—H15C | 109.5 |
| O1—C4—N1 | 120.22 (17) | N3—C7—H7A | 109.5 |
| N3—C4—N1 | 114.97 (15) | N3—C7—H7B | 109.5 |
| C5—N6—C8 | 120.58 (16) | H7A—C7—H7B | 109.5 |
| C5—N6—H6 | 119.7 | N3—C7—H7C | 109.5 |
| C8—N6—H6 | 119.7 | H7A—C7—H7C | 109.5 |
| C13—N9—C15 | 120.93 (16) | H7B—C7—H7C | 109.5 |
| C13—N9—H9 | 119.5 | N6—C8—H8A | 109.5 |
| C15—N9—H9 | 119.5 | N6—C8—H8B | 109.5 |
| O4—C14—N12 | 124.41 (16) | H8A—C8—H8B | 109.5 |
| O4—C14—N10 | 120.80 (16) | N6—C8—H8C | 109.5 |
| N12—C14—N10 | 114.76 (15) | H8A—C8—H8C | 109.5 |
| N2—C3—N4 | 120.34 (16) | H8B—C8—H8C | 109.5 |
| N2—C3—C1 | 117.75 (17) | N12—C16—H16A | 109.5 |
| N4—C3—C1 | 121.85 (16) | N12—C16—H16B | 109.5 |
| O3—C13—N9 | 124.37 (17) | H16A—C16—H16B | 109.5 |
| O3—C13—N7 | 120.74 (17) | N12—C16—H16C | 109.5 |
| N9—C13—N7 | 114.83 (16) | H16A—C16—H16C | 109.5 |
| N5—C6—N1 | 120.09 (15) | H16B—C16—H16C | 109.5 |

| | | | |
|---|---|---|---|
| C6—N5—N4—C3 | 33.9 (2) | C6—N1—C4—N3 | 162.35 (16) |
| C6—N5—N4—C5 | −166.36 (15) | N2—N1—C4—N3 | 7.1 (2) |
| C6—N1—N2—C3 | 33.9 (2) | O2—C5—N6—C8 | −5.5 (3) |
| C4—N1—N2—C3 | −168.75 (16) | N4—C5—N6—C8 | 172.64 (16) |
| C12—N11—N10—C9 | 31.0 (2) | C16—N12—C14—O4 | 1.3 (3) |
| C12—N11—N10—C14 | −159.33 (16) | C16—N12—C14—N10 | 179.32 (17) |
| C9—N8—N7—C12 | 32.6 (2) | C9—N10—C14—O4 | −8.9 (3) |
| C9—N8—N7—C13 | −165.91 (16) | N11—N10—C14—O4 | −177.71 (15) |

| | | | |
|---|---|---|---|
| C3—N4—C5—O2 | −25.0 (3) | C9—N10—C14—N12 | 172.96 (16) |
| N5—N4—C5—O2 | 176.99 (15) | N11—N10—C14—N12 | 4.2 (2) |
| C3—N4—C5—N6 | 156.80 (16) | N1—N2—C3—N4 | −4.4 (2) |
| N5—N4—C5—N6 | −1.2 (2) | N1—N2—C3—C1 | 178.52 (17) |
| N7—N8—C9—N10 | −6.1 (2) | C5—N4—C3—N2 | 172.45 (16) |
| N7—N8—C9—C10 | 177.08 (15) | N5—N4—C3—N2 | −29.7 (2) |
| C14—N10—C9—N8 | 165.74 (17) | C5—N4—C3—C1 | −10.6 (3) |
| N11—N10—C9—N8 | −25.7 (2) | N5—N4—C3—C1 | 147.23 (18) |
| C14—N10—C9—C10 | −17.6 (3) | C15—N9—C13—O3 | 1.0 (3) |
| N11—N10—C9—C10 | 150.96 (17) | C15—N9—C13—N7 | 178.38 (17) |
| N10—N11—C12—N7 | −4.4 (2) | C12—N7—C13—O3 | −19.3 (3) |
| N10—N11—C12—C11 | 177.61 (16) | N8—N7—C13—O3 | −179.19 (17) |
| C13—N7—C12—N11 | 173.17 (17) | C12—N7—C13—N9 | 163.24 (17) |
| N8—N7—C12—N11 | −27.3 (2) | N8—N7—C13—N9 | 3.3 (2) |
| C13—N7—C12—C11 | −8.9 (3) | N4—N5—C6—N1 | −4.2 (2) |
| N8—N7—C12—C11 | 150.58 (17) | N4—N5—C6—C2 | 176.52 (15) |
| C7—N3—C4—O1 | 4.1 (3) | C4—N1—C6—N5 | 175.41 (16) |
| C7—N3—C4—N1 | −178.51 (17) | N2—N1—C6—N5 | −29.7 (2) |
| C6—N1—C4—O1 | −20.2 (3) | C4—N1—C6—C2 | −5.3 (3) |
| N2—N1—C4—O1 | −175.36 (16) | N2—N1—C6—C2 | 149.51 (17) |

*Hydrogen-bond geometry (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N3—H3···N2 | 0.86 | 2.16 | 2.572 (2) | 108 |
| N6—H6···N5 | 0.86 | 2.19 | 2.586 (2) | 108 |
| N9—H9···N8 | 0.86 | 2.15 | 2.567 (2) | 109 |
| N12—H12···N11 | 0.86 | 2.17 | 2.581 (2) | 109 |
| N3—H3···O4 | 0.86 | 2.20 | 2.925 (2) | 142 |
| N6—H6···O3$^{i}$ | 0.86 | 2.16 | 2.918 (2) | 146 |
| N9—H9···O1$^{ii}$ | 0.86 | 2.14 | 2.877 (3) | 143 |
| N12—H12···O2$^{iii}$ | 0.86 | 2.24 | 2.967 (3) | 142 |

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