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2,3-Diaminophenazine tetrahydrate

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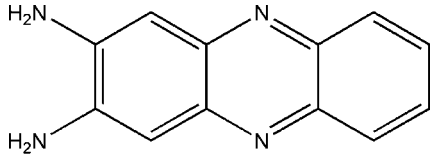
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.004 Å; R factor = 0.048; wR factor = 0.140; data-to-parameter ratio = 7.1.

The title compound, $C_{12}H_{10}N_4\cdot 4H_2O$, was obtained from a room-temperature solution of *o*-phenylenediamine and copper acetate. In the crystal structure, there are significant π–π stacking interactions, with a centroid–centroid separation of 3.575 (2) Å. In addition, intermolecular O—H···O, N—H···O, N—H···N and O—H···N hydrogen bonds link 2,3-diaminophenazine molecules and water molecules, forming a three-dimensional framework.

Related literature

For related literature, see: Brownstein & Enright (1995); Doyle *et al.* (2001); Chłopek *et al.* (2005).



$4H_2O$

Experimental

Crystal data

$C_{12}H_{10}N_4\cdot 4H_2O$
M_r = 282.30
Orthorhombic, $Pca2_1$
a = 16.7593 (18) Å
b = 18.1200 (19) Å
c = 4.7834 (5) Å
V = 1452.6 (3) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.10 mm^{-1}
T = 293 (2) K
0.37 × 0.32 × 0.23 mm

Data collection

Bruker SMART APEX area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.965, T_{max} = 0.977
7735 measured reflections
1608 independent reflections
1432 reflections with $I > 2\sigma(I)$
R_{int} = 0.022

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.048
$wR(F^2)$ = 0.140
S = 1.14
1608 reflections
225 parameters
17 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.29 e Å^{-3}
$\Delta\rho_{min}$ = −0.12 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N4—H4B···O2W^{i}	0.895 (10)	2.218 (12)	3.105 (5)	171 (3)
N4—H4C···N4^{ii}	0.90 (3)	2.58 (3)	3.198 (3)	126 (3)
N3—H3B···O1W^{iii}	0.906 (10)	2.165 (16)	3.048 (6)	165 (4)
N3—H3C···N3^{ii}	0.895 (11)	2.33 (2)	3.122 (4)	147 (3)
O4W—H4WA···O4W^{iv}	0.855 (19)	2.017 (19)	2.871 (3)	176 (4)
O4W—H4WB···N2	0.867 (17)	1.924 (19)	2.787 (3)	173 (4)
O3W—H3WB···N1	0.872 (19)	1.96 (3)	2.801 (3)	161 (6)
O2W—H2WA···O4W^{v}	0.84 (2)	2.01 (2)	2.843 (4)	178 (5)
O1W—H1WA···O1W^{vi}	0.84 (6)	2.15 (6)	2.860 (7)	142 (6)
O2W—H2WB···O2W^{vii}	0.87 (4)	1.97 (4)	2.812 (5)	161 (3)
O1W—H1WB···O3W	0.85 (3)	2.09 (3)	2.882 (6)	155 (5)

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

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: LH2601).

References

Brownstein, S. K. & Enright, G. D. (1995). *Acta Cryst.* C**51**, 1579–1581.
Bruker (2001). *SAINT* and *SMART*. Bruker AXS Inc., Madison, Wisconsin, USA.
Chłopek, K., Bill, E., Weyhermüller, T. & Wieghardt, K. (2005). *Inorg. Chem.* **44**, 7087–7098.
Doyle, R. P., Kruger, P. E., Mackie, P. R. & Nieuwenhuyzen, M. (2001). *Acta Cryst.* C**57**, 104–105.
Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

supporting information

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2,3-Diaminophenazine tetrahydrate

Xiao-Feng Li, Yan An and Yan-Sheng Yin

S1. Comment

The crystal structures of phenazinediamine (Doyle, *et al.*, 2001) and examples of its derivatives (Brownstein, *et al.*, 1995; Krzysztof, *et al.*, 2005) have been published. As part of our studies of these types of compounds we report here the crystal structure of the title compound (I) which was synthesized at room temperature using *o*-Phenylenediamine and copper acetate.

In compound (I), the asymmetric unit contains a 2,3-Diamino-phenazine molecule and four water molecules (Fig. 1). In the crystal structure, 2,3-Diamino-phenazine molecules related by unit cell translations along the *c* axis form moderately strong $\pi\cdots\pi$ stacking interactions (*Cg*1$\cdots$.*Cg*2(x, y, -1 + z) and *Cg*1$\cdots$*Cg*3(x, y, 1 + z) = 3.575 (2) Å, where *Cg*1, *Cg*2 and *Cg*3 are the centroids defined by ring atoms N1/N2/C1/C6/C9/C10, C1—C6 and C7—C12, respectively). In addition, water molecules and 2,3-Diamino-phenazine molecules are linked by O—H···N, O—H···O, N—H···N and H—H···O hydrogen bonds to form a three-dimensional network (Table 1 & Fig.2).

S2. Experimental

A mixture of *o*-Phenylenediamine(0.5 mmol, 0.054 g), $Cu(CH_3COO)_2$ (0.5 mmol,0.099 g), NaOH (1 mmol, 0.04 g), and water (10 ml) was placed in a 20 ml vial, stirring in air for 1 h. It was then sealed for 1 week and the resulting black block-shaped single crystals were collected. Yield: 67%. C&H analysis for $C_{12}H_{18}N_4O_4$ (found/calc): C, 51.03(51.06), H, 6.39(6.43).

S3. Refinement

In the absence of significant anomalous dispersion effects the Friedel pairs were merged. The H atoms were placed in calculated positions in the riding-model approximation (C—H 0.93 Å, N—H 0.90 Å), with their temperature factors were set to 1.2 times those of the equivalent isotropic temperature factors of the parent atoms. The water H atoms were located in difference Fourier maps and refined isotropically with distance restrains of O—H = 0.85 (2) and H···H = 1.39 (1) Å.

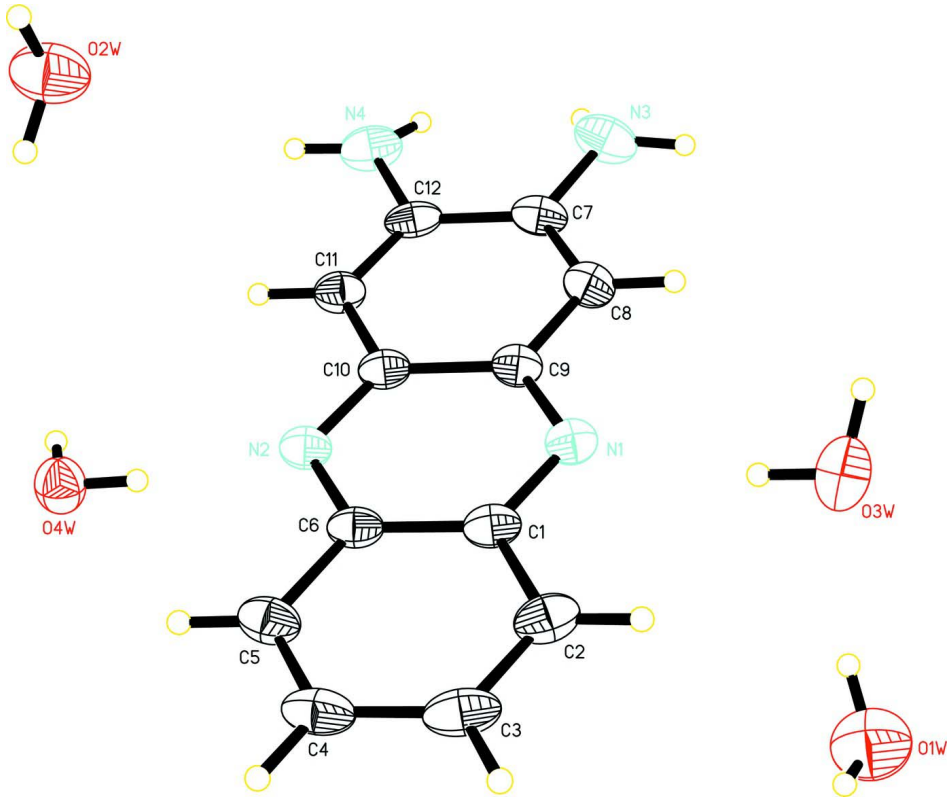

Figure 1

The asymmetric unit of (I).

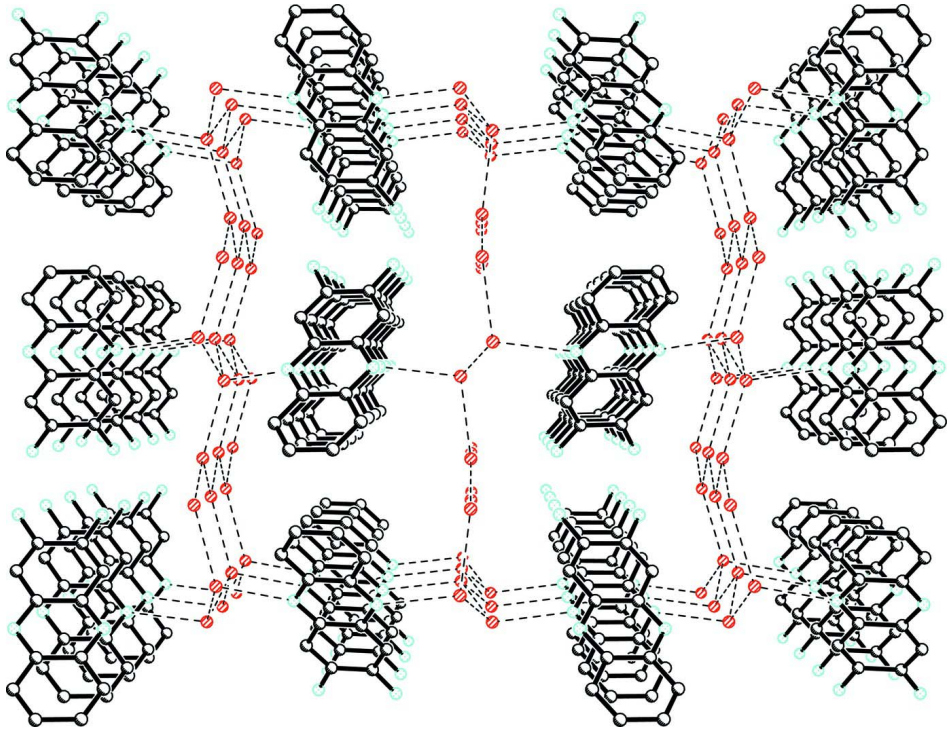

Figure 2

Part of the crystal structure viewed along the *c*-axis. Dashed lines are drawn between the donor and acceptor atoms of the hydrogen bonds but H atoms are not showm.

2,3-Diaminophenazine tetrahydrate

Crystal data

$C_{12}H_{10}N_4 \cdot 4H_2O$
$M_r = 282.30$
Orthorhombic, $Pca2_1$
Hall symbol: P 2c -2ac
$a = 16.7593\ (18)$ Å
$b = 18.1200\ (19)$ Å
$c = 4.7834\ (5)$ Å
$V = 1452.6\ (3)$ Å^3
$Z = 4$
$F(000) = 600$
$D_x = 1.291$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 3569 reflections
$\theta = 2.7–24.3°$
$\mu = 0.10$ mm^{-1}
$T = 293$ K
Block, black
0.37 × 0.32 × 0.23 mm

Data collection

Bruker SMART APEX area-detector diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.965$, $T_{max} = 0.977$
7735 measured reflections
1608 independent reflections
1432 reflections with $I > 2\sigma(I)$
$R_{int} = 0.022$
$\theta_{max} = 26.0°$, $\theta_{min} = 1.1°$
$h = -20 \rightarrow 18$
$k = -19 \rightarrow 22$
$l = -5 \rightarrow 5$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.048$
$wR(F^2) = 0.140$
$S = 1.14$
1608 reflections
225 parameters
17 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0963P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.29$ e Å^{-3}
$\Delta\rho_{min} = -0.12$ 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 (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
N1	0.51508 (13)	0.31719 (12)	0.3965 (5)	0.0417 (6)
N2	0.51933 (12)	0.16406 (12)	0.2821 (6)	0.0410 (5)
C10	0.46946 (14)	0.20894 (15)	0.1460 (6)	0.0393 (6)
C11	0.41763 (15)	0.18021 (16)	−0.0623 (7)	0.0443 (7)
H11A	0.4184	0.1299	−0.1008	0.053*
C1	0.56542 (15)	0.27142 (16)	0.5338 (6)	0.0418 (7)
C12	0.36660 (15)	0.22488 (17)	−0.2076 (6)	0.0445 (7)
C8	0.41408 (16)	0.33188 (16)	0.0507 (7)	0.0456 (7)
H8A	0.4123	0.3823	0.0873	0.055*
C9	0.46739 (15)	0.28738 (15)	0.2042 (6)	0.0394 (6)
N4	0.31334 (15)	0.19700 (17)	−0.3960 (7)	0.0603 (8)
H4B	0.3134 (18)	0.1476 (6)	−0.403 (10)	0.072*
H4C	0.2916 (19)	0.2287 (16)	−0.520 (7)	0.072*
N3	0.30987 (17)	0.34664 (19)	−0.2858 (6)	0.0630 (8)
H3B	0.315 (2)	0.3961 (7)	−0.263 (12)	0.076*
H3C	0.2912 (19)	0.333 (2)	−0.454 (4)	0.076*
C5	0.62032 (15)	0.14891 (17)	0.6301 (7)	0.0498 (7)
H5A	0.6222	0.0985	0.5942	0.060*
C6	0.56701 (14)	0.19474 (15)	0.4760 (6)	0.0401 (6)
C2	0.61674 (16)	0.30014 (19)	0.7428 (7)	0.0512 (8)
H2A	0.6163	0.3504	0.7828	0.061*
C7	0.36499 (15)	0.30342 (16)	−0.1501 (6)	0.0446 (7)
C4	0.66820 (16)	0.1785 (2)	0.8286 (7)	0.0561 (8)
H4A	0.7025	0.1480	0.9289	0.067*

C3	0.66680 (18)	0.25428 (18)	0.8851 (7)	0.0576 (9)
H3A	0.7004	0.2736	1.0213	0.069*
O4W	0.54392 (14)	0.01642 (12)	0.1437 (6)	0.0592 (6)
O3W	0.53446 (19)	0.47020 (15)	0.4439 (8)	0.0798 (8)
O2W	0.29410 (18)	0.02670 (19)	0.5763 (7)	0.0818 (8)
O1W	0.7032 (3)	0.4897 (3)	0.3542 (10)	0.1042 (11)
H4WB	0.541 (2)	0.0631 (11)	0.182 (8)	0.088 (14)*
H3WB	0.535 (3)	0.4238 (14)	0.396 (16)	0.16 (3)*
H4WA	0.516 (2)	0.0085 (18)	−0.004 (7)	0.070 (12)*
H3WA	0.4832 (14)	0.481 (2)	0.455 (16)	0.14 (2)*
H2WA	0.3416 (11)	0.014 (2)	0.601 (11)	0.102 (16)*
H1WA	0.723 (3)	0.469 (4)	0.495 (12)	0.22 (4)*
H2WB	0.266 (2)	0.016 (2)	0.724 (8)	0.093 (16)*
H1WB	0.6547 (14)	0.478 (2)	0.330 (13)	0.11 (2)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0396 (11)	0.0510 (12)	0.0344 (13)	−0.0021 (9)	0.0026 (10)	−0.0015 (11)
N2	0.0359 (11)	0.0526 (12)	0.0346 (12)	0.0009 (9)	0.0026 (11)	−0.0002 (11)
C10	0.0319 (12)	0.0550 (14)	0.0311 (14)	−0.0024 (10)	0.0056 (12)	0.0001 (12)
C11	0.0373 (13)	0.0571 (15)	0.0386 (15)	−0.0018 (12)	−0.0006 (13)	−0.0059 (13)
C1	0.0337 (13)	0.0606 (16)	0.0309 (15)	−0.0032 (11)	0.0033 (11)	0.0012 (12)
C12	0.0302 (13)	0.0741 (18)	0.0293 (14)	−0.0081 (12)	0.0057 (11)	−0.0011 (14)
C8	0.0444 (14)	0.0551 (14)	0.0375 (16)	0.0061 (12)	0.0035 (13)	0.0010 (13)
C9	0.0361 (12)	0.0509 (14)	0.0313 (16)	0.0018 (11)	0.0035 (11)	−0.0008 (12)
N4	0.0465 (14)	0.092 (2)	0.0428 (16)	−0.0086 (13)	−0.0108 (13)	−0.0011 (17)
N3	0.0539 (15)	0.089 (2)	0.0463 (17)	0.0191 (14)	−0.0071 (14)	0.0025 (15)
C5	0.0394 (13)	0.0697 (17)	0.0401 (17)	0.0079 (12)	0.0028 (13)	0.0071 (16)
C6	0.0303 (12)	0.0586 (15)	0.0315 (15)	−0.0004 (10)	0.0021 (12)	0.0022 (13)
C2	0.0423 (15)	0.0733 (18)	0.0379 (17)	−0.0112 (13)	0.0007 (13)	−0.0048 (16)
C7	0.0357 (13)	0.0699 (18)	0.0282 (15)	0.0063 (12)	0.0034 (12)	0.0024 (13)
C4	0.0358 (14)	0.090 (2)	0.0421 (18)	0.0057 (15)	−0.0020 (13)	0.0131 (17)
C3	0.0379 (15)	0.098 (3)	0.0366 (16)	−0.0096 (15)	−0.0058 (14)	0.0019 (17)
O4W	0.0671 (14)	0.0536 (12)	0.0569 (15)	0.0009 (10)	−0.0081 (13)	0.0014 (12)
O3W	0.103 (2)	0.0588 (14)	0.078 (2)	−0.0099 (13)	−0.003 (2)	−0.0042 (14)
O2W	0.0642 (17)	0.118 (2)	0.0636 (18)	0.0089 (16)	−0.0007 (16)	0.0027 (17)
O1W	0.097 (2)	0.123 (3)	0.092 (3)	−0.006 (2)	0.007 (2)	0.011 (2)

Geometric parameters (Å, º)

N1—C9	1.333 (3)	N3—H3B	0.906 (10)
N1—C1	1.353 (3)	N3—H3C	0.895 (11)
N2—C10	1.335 (3)	C5—C4	1.353 (5)
N2—C6	1.345 (4)	C5—C6	1.425 (4)
C10—C11	1.421 (4)	C5—H5A	0.9300
C10—C9	1.449 (4)	C2—C3	1.363 (4)
C11—C12	1.367 (4)	C2—H2A	0.9300

C11—H11A	0.9300	C4—C3	1.400 (4)
C1—C6	1.417 (4)	C4—H4A	0.9300
C1—C2	1.417 (4)	C3—H3A	0.9300
C12—N4	1.366 (4)	O4W—H4WB	0.867 (17)
C12—C7	1.450 (4)	O4W—H4WA	0.855 (19)
C8—C7	1.366 (4)	O3W—H3WB	0.872 (19)
C8—C9	1.410 (4)	O3W—H3WA	0.883 (19)
C8—H8A	0.9300	O2W—H2WA	0.837 (19)
N4—H4B	0.895 (10)	O2W—H2WB	0.87 (4)
N4—H4C	0.90 (3)	O1W—H1WA	0.84 (6)
N3—C7	1.374 (4)	O1W—H1WB	0.849 (18)

C9—N1—C1	117.4 (2)	C7—N3—H3C	120 (3)
C10—N2—C6	117.2 (2)	H3B—N3—H3C	114 (4)
N2—C10—C11	120.1 (2)	C4—C5—C6	120.3 (3)
N2—C10—C9	121.2 (2)	C4—C5—H5A	119.9
C11—C10—C9	118.7 (2)	C6—C5—H5A	119.9
C12—C11—C10	121.5 (3)	N2—C6—C1	121.9 (2)
C12—C11—H11A	119.3	N2—C6—C5	119.2 (3)
C10—C11—H11A	119.3	C1—C6—C5	118.8 (2)
N1—C1—C6	121.2 (2)	C3—C2—C1	120.1 (3)
N1—C1—C2	119.7 (3)	C3—C2—H2A	119.9
C6—C1—C2	119.1 (3)	C1—C2—H2A	119.9
N4—C12—C11	121.7 (3)	C8—C7—N3	121.5 (3)
N4—C12—C7	118.4 (3)	C8—C7—C12	119.5 (3)
C11—C12—C7	119.8 (3)	N3—C7—C12	118.9 (3)
C7—C8—C9	122.2 (3)	C5—C4—C3	120.9 (3)
C7—C8—H8A	118.9	C5—C4—H4A	119.6
C9—C8—H8A	118.9	C3—C4—H4A	119.6
N1—C9—C8	120.5 (3)	C2—C3—C4	120.8 (3)
N1—C9—C10	121.1 (2)	C2—C3—H3A	119.6
C8—C9—C10	118.4 (2)	C4—C3—H3A	119.6
C12—N4—H4B	113 (3)	H4WB—O4W—H4WA	108 (2)
C12—N4—H4C	118 (2)	H3WB—O3W—H3WA	105 (2)
H4B—N4—H4C	128 (4)	H2WA—O2W—H2WB	109 (2)
C7—N3—H3B	117 (3)	H1WA—O1W—H1WB	112 (3)

C6—N2—C10—C11	179.8 (2)	N1—C1—C6—N2	0.5 (4)
C6—N2—C10—C9	0.4 (4)	C2—C1—C6—N2	179.4 (3)
N2—C10—C11—C12	−179.2 (2)	N1—C1—C6—C5	−179.0 (3)
C9—C10—C11—C12	0.2 (4)	C2—C1—C6—C5	0.0 (4)
C9—N1—C1—C6	−0.3 (4)	C4—C5—C6—N2	−179.2 (3)
C9—N1—C1—C2	−179.2 (2)	C4—C5—C6—C1	0.2 (4)
C10—C11—C12—N4	−176.0 (3)	N1—C1—C2—C3	179.0 (3)
C10—C11—C12—C7	0.2 (4)	C6—C1—C2—C3	0.0 (4)
C1—N1—C9—C8	−179.3 (2)	C9—C8—C7—N3	175.9 (3)
C1—N1—C9—C10	0.2 (4)	C9—C8—C7—C12	0.6 (4)
C7—C8—C9—N1	179.2 (2)	N4—C12—C7—C8	175.8 (3)

C7—C8—C9—C10	−0.2 (4)	C11—C12—C7—C8	−0.6 (4)
N2—C10—C9—N1	−0.3 (3)	N4—C12—C7—N3	0.4 (4)
C11—C10—C9—N1	−179.6 (3)	C11—C12—C7—N3	−176.0 (3)
N2—C10—C9—C8	179.2 (3)	C6—C5—C4—C3	−0.5 (4)
C11—C10—C9—C8	−0.2 (3)	C1—C2—C3—C4	−0.3 (5)
C10—N2—C6—C1	−0.5 (4)	C5—C4—C3—C2	0.5 (5)
C10—N2—C6—C5	179.0 (2)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N4—H4*B*···O2*W*^{i}	0.90 (1)	2.22 (1)	3.105 (5)	171 (3)
N4—H4*C*···N4^{ii}	0.90 (3)	2.58 (3)	3.198 (3)	126 (3)
N3—H3*B*···O1*W*^{iii}	0.91 (1)	2.17 (2)	3.048 (6)	165 (4)
N3—H3*C*···N3^{ii}	0.90 (1)	2.33 (2)	3.122 (4)	147 (3)
O4*W*—H4*WA*···O4*W*^{iv}	0.86 (2)	2.02 (2)	2.871 (3)	176 (4)
O4*W*—H4*WB*···N2	0.87 (2)	1.92 (2)	2.787 (3)	173 (4)
O3*W*—H3*WB*···N1	0.87 (2)	1.96 (3)	2.801 (3)	161 (6)
O2*W*—H2*WA*···O4*W*^{v}	0.84 (2)	2.01 (2)	2.843 (4)	178 (5)
O1*W*—H1*WA*···O1*W*^{vi}	0.84 (6)	2.15 (6)	2.860 (7)	142 (6)
O2*W*—H2*WB*···O2*W*^{vii}	0.87 (4)	1.97 (4)	2.812 (5)	161 (3)
O1*W*—H1*WB*···O3*W*	0.85 (3)	2.09 (3)	2.882 (6)	155 (5)

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