Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

1,1′-(4-Oxoheptane-1,7-diyl)bis(2-methyl-1*H*-benzimidazole) pentahydrate

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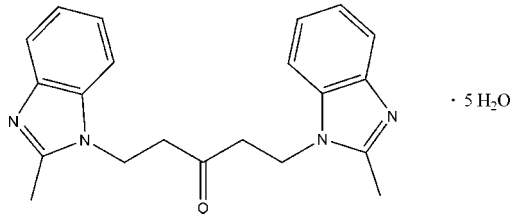
Received 30 October 2007; accepted 25 November 2007

Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.006 Å; R factor = 0.079; wR factor = 0.222; data-to-parameter ratio = 14.2.

The title compound, $C_{23}H_{26}N_4O\cdot5H_2O$, has noncrystallographic twofold rotation symmetry in the solid state. It crystallizes with five solvent water molecules in the asymmetric unit. Four of these water molecules are connected with each other *via* hydrogen-bonding interactions to form two types of centrosymmetric hexameric $(H_2O)_6$ rings. *Via* edge sharing of the hexamers, the water clusters thus build infinite chains that stretch parallel to the *a* axis. The fifth water molecule provides an additional connection between the two hexameric $(H_2O)_6$ units *via* hydrogen bonds to both rings. The water molecules in the channels along the *a* axis are also bonded *via* O—H···N hydrogen bonds to the organic units, and face-to-face π–π interactions [with centroid-to-centroid distances of 3.656 (1) Å and average face-to-face distances of 3.431 (5) Å] between the aromatic rings of adjacent molecules complete the intermolecular interactions in this structure.

Related literature

Hay *et al.* (1998) report the use of benzimidazole complexes to model the active site of a variety of metalloenzymes, such as carbonic anhydrase and carboxypeptidase.



Experimental

Crystal data

$C_{23}H_{26}N_4O\cdot5H_2O$
M_r = 464.56
Monoclinic, $P2_1/n$
a = 8.814 (5) Å
b = 25.664 (13) Å
c = 11.635 (6) Å
β = 109.06 (1)°
V = 2488 (2) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.09 mm^{-1}
T = 293 (2) K
0.40 × 0.30 × 0.25 mm

Data collection

Bruker APEX CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.970, T_{max} = 0.982
12521 measured reflections
4424 independent reflections
2623 reflections with $I > 2\sigma(I)$
R_{int} = 0.109

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.079
$wR(F^2)$ = 0.222
S = 1.01
4424 reflections
311 parameters
15 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.33 e Å^{-3}
$\Delta\rho_{min}$ = −0.27 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
O1W—H1A···N4	0.93 (2)	1.95 (4)	2.758 (6)	144 (5)
O1W—H1B···O3W^{i}	0.92 (4)	2.31 (5)	2.954 (5)	127 (5)
O2W—H2B···O4W	0.90 (5)	2.61 (6)	3.308 (7)	135 (7)
O2W—H2B···O5W^{ii}	0.90 (5)	2.05 (7)	2.770 (6)	136 (8)
O3W—H3B···O1^{iii}	0.88 (5)	2.18 (5)	3.054 (6)	171 (7)
O4W—H4B···O1W^{i}	0.92 (8)	2.00 (7)	2.900 (7)	166 (8)
O4W—H4A···O5W^{ii}	0.92 (7)	2.33 (4)	3.200 (7)	157 (7)
O5W—H5B···N1^{iv}	0.90 (5)	1.93 (5)	2.822 (5)	175 (6)
O5W—H5A···O3W^{v}	0.90 (6)	1.92 (6)	2.811 (6)	167 (6)
O3W—H3A···O2W^{i}	0.91 (2)	1.94 (2)	2.840 (7)	170 (6)
O2W—H2A···O1W^{i}	0.90 (2)	2.14 (5)	2.823 (6)	132 (5)

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

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL-Plus* (Sheldrick, 1990); software used to prepare material for publication: *SHELXL97*.

We thank the Science Foundation for Young Teachers of Northeast Normal University (No. 20070314) for support.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: ZL2082).

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supporting information

Acta Cryst. (2008). E**64**, o143 [https://doi.org/10.1107/S1600536807063039]

1,1′-(4-Oxoheptane-1,7-diyl)bis(2-methyl-1*H*-benzimidazole) pentahydrate

Lai-Ping Zhang, Ying-Ying Liu, Zhi-Fang Jia and Guo-Hua Wei

S1. Comment

Currently there is considerable interest in the use of benzimidazole complexes to model the active site of a variety of metalloenzymes such as carbonic anhydrase and carboxypeptidase (Hay *et al.*, 1998). In this context we prepared (Fig 4) and analyzed the title benzimidazole compound, and its structure is described here.

The title molecule (Fig 1) has non-crystallographic two fold symmetry with an r.m.s. deviation for both halves of 0.066 Å. It crystallizes with five lattice water molecules in the asymmetric part of the unit cell. Four of these water molecules (O1W, O2W, O3W and O5W) are connected with each other *via* hydrogen bonding interactions to form two types of centrosymmetric hexameric $(H_2O)_6$ rings. Via edge sharing of the hexamers the water clusters thus build infinite chains that stretch parallel to the *a* axis. The fifth water molecule O4W provides an additional connection between the two hexameric $(H_2O)_6$ rings *via* hydrogen bonds to both units. Water molecules O1W and O5W in the channels along *a* axis are also bonded *via* O—H···N hydrogen bonds to N4 and N1 of the organic unit, and all water molecules act both as donors and acceptors (Fig. 2).

Face-to-face π-π interactions between adjacent benzimidazoles made up by the atoms C1—C7, N3 and N4 and their symmetry equivalents at 1 - *x*, -*y*, 2 - *z* (with centroid-to-centriod distances of 3.656 (1) Å and an average face-to-face distance of 3.431 (5) Å, Fig. 3) complete the intermolecular interactions in this structure and lead to the formation of a 1-D supramolecuar chain along the *a* axis.

S2. Experimental

To a solution of 1,7-dichloro-4-oxoheptane (8.3 g, 47 mmol) and ethylene glycol (2.9 g, 47 mmol) in cyclohexane (35 ml) was added 0.024 g sodium bisulfate. The reaction mixture was refluxed for 3 h with azeotropic removal of water *via* a Dean–Stark trap, until there was no more water created. The resulting clear solution was cooled down, washed with water twice, and then distilled. The fraction distilling between 447 K and 453 K was collected to obtain 1,11-dichloro-(5,8-dioxaspiro[4.2]undecane) as a clear liquid (5.5 g, 25 mmol, 53%).

A mixture of 2-methyl-benzimidazole (6.6 g, 50 mmol) and NaOH (2.0 g, 50 mmol) in DMSO (10 ml) was stirred at 333 K for 1 h, and then the collected distillate (5.5 g, 25 mmol) from the previous step was added. The mixture was cooled to room temperature after stirring at 333 K for 2 h, then poured into 200 ml of water and a white solid formed immediately. The compound (5,8-dioxaspiro[4.2]undecyl)bis(2-methyl-benzimidazole) was obtained in 74% yield (7.6 g, 19 mmol).

After washing with 50 ml water, the solid was transfered into 150 ml water with 10 ml HCl (12 mol l^{-1}). The mixture was refluxed for 3.5 h, and then filtered. The obtained residue was dissolved in 100 ml me thanol, and colorless single crystals of the title compound were obtained after several days at room temperature (3.7 g, 10 mmol, 55%).

S3. Refinement

The methyl H atoms were refined as members of rigid groups with C—H = 0.96 Å and U_{iso}(H) = 1.5U_{eq}(parent atom), and were allowed to rotate around the C—C bonds. Other H atoms on C atoms were positioned geometrically and refined as riding atoms, with C—H = 0.93 Å and U_{iso}(H) = 1.2U_{eq}(parent atom). Water H atoms were located in a difference Fourier map and refined as riding atoms, with an O—H distance of 0.89 (2) Å, and with U_{iso}(H) = 1.5U_{eq}(O). An anti-bumping restraint (standard deviation 0.01 Å) was used to avoid chemically not meaningful close contacts between the hydrogen atoms of the water molecules.

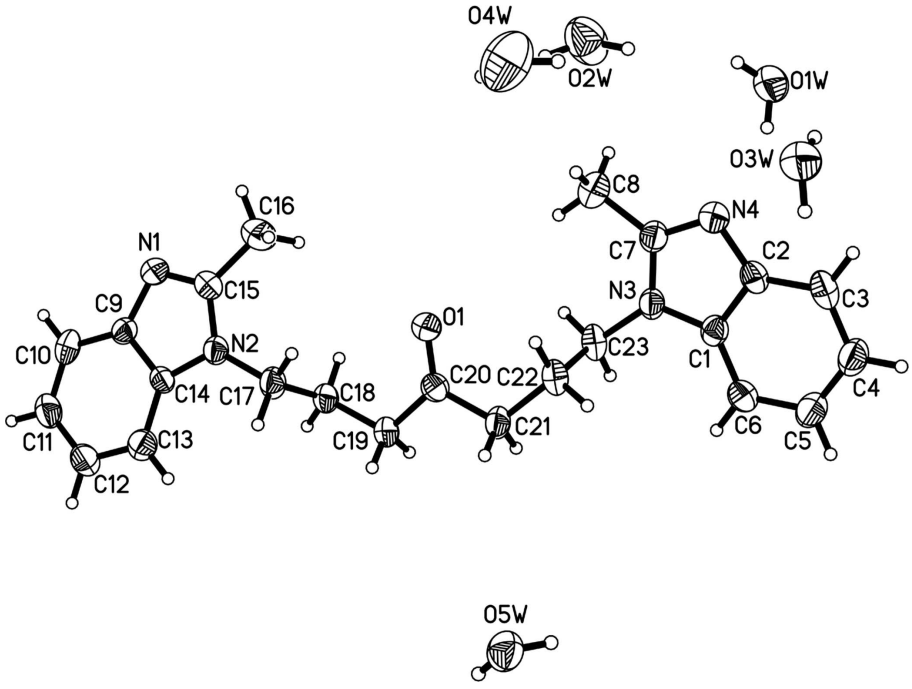

Figure 1

View of the structure of the title compound. Displacement ellipsoids are drawn at the 30% probability level.

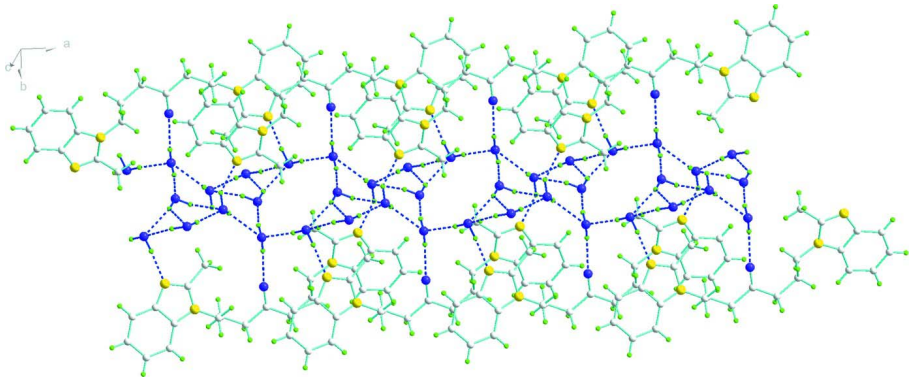

Figure 2

The water filled channels along the *a* axis. Hydrogen bonds are represented by dashed lines.

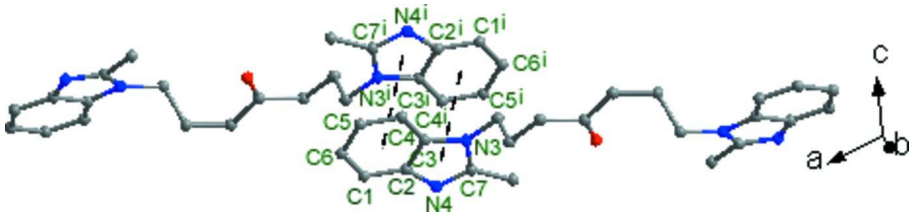

Figure 3

The π-π interactions in the structure of the title compound. H atoms have been omitted for clarity. Symmetry codes: (i) 1 - *x*, -*y*, 2 - *z*.

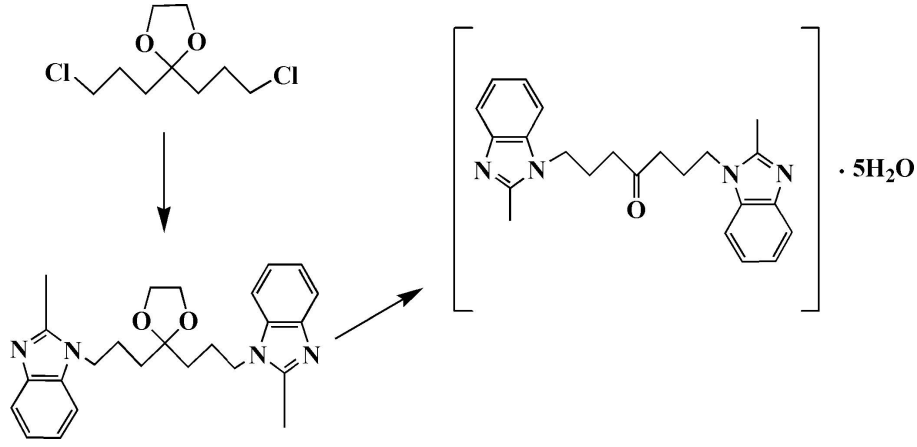

Figure 4

The synthesis of the title compound as described in the experimental section.

1,1′-(4-Oxoheptane-1,7-diyl)bis(2-methyl-1*H*-benzimidazole) pentahydrate

Crystal data

$C_{23}H_{26}N_4O·5H_2O$
$M_r = 464.56$
Monoclinic, $P2_1/n$
Hall symbol: -P 2yn
$a = 8.814$ (5) Å
$b = 25.664$ (13) Å
$c = 11.635$ (6) Å
$\beta = 109.06$ (1)°
$V = 2488$ (2) Å^3
$Z = 4$
$F(000) = 1000$
$D_x = 1.240$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 4407 reflections
$\theta = 1.6$–25.3°
$\mu = 0.09$ mm^{-1}
$T = 293$ K
Block, colorless
0.40 × 0.30 × 0.25 mm

Data collection

Bruker APEX CCD area-detector diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
ω scans
Absorption correction: empirical (using intensity measurements) (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.970$, $T_{max} = 0.982$
12521 measured reflections
4424 independent reflections
2623 reflections with $I > 2\sigma(I)$
$R_{int} = 0.109$
$\theta_{max} = 25.3°$, $\theta_{min} = 1.6°$
$h = -10 \rightarrow 10$
$k = -24 \rightarrow 30$
$l = -13 \rightarrow 13$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.079$
$wR(F^2) = 0.222$
$S = 1.01$
4424 reflections
311 parameters
15 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
$w = 1/[\sigma^2(F_o^2) + (0.0646P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.33$ e Å^{-3}
$\Delta\rho_{min} = -0.27$ e Å^{-3}
Extinction correction: *SHELXL97*, $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.011 (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 (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.7657 (6)	0.03465 (19)	0.9184 (5)	0.0691 (15)
H1	0.8154	0.0179	0.8693	0.083*
C2	0.6000 (5)	0.03845 (18)	0.8828 (4)	0.0554 (13)
C3	0.5296 (5)	0.06379 (18)	0.9592 (4)	0.0551 (13)
C4	0.6183 (6)	0.08559 (19)	1.0686 (5)	0.0670 (14)
H4	0.5697	0.1026	1.1180	0.080*
C5	0.7824 (7)	0.0810 (2)	1.1012 (5)	0.0804 (17)
H5	0.8467	0.0950	1.1747	0.096*
C6	0.8542 (6)	0.0558 (2)	1.0266 (6)	0.0785 (17)
H6	0.9655	0.0534	1.0513	0.094*
C7	0.3447 (6)	0.0363 (2)	0.7922 (4)	0.0603 (13)
C8	0.1824 (2)	0.02679 (8)	0.70124 (17)	0.0900 (19)
H8A	0.1014	0.0396	0.7326	0.135*
H8B	0.1675	−0.0099	0.6858	0.135*
H8C	0.1742	0.0446	0.6269	0.135*
C9	−0.8388 (2)	0.22467 (8)	0.63617 (17)	0.0538 (13)
C10	−0.9846 (2)	0.24529 (8)	0.63617 (17)	0.0691 (15)
H10	−1.0804	0.2309	0.5863	0.083*
C11	−0.9873 (2)	0.28737 (8)	0.71070 (17)	0.0743 (16)
H11	−1.0849	0.3012	0.7107	0.089*
C12	−0.8442 (2)	0.30882 (8)	0.78523 (17)	0.0753 (16)
H12	−0.8460	0.3370	0.8351	0.090*
C13	−0.6984 (2)	0.28820 (8)	0.78522 (17)	0.0648 (14)

H13	−0.6027	0.3026	0.8351	0.078*
C14	−0.6957 (2)	0.24613 (8)	0.71069 (17)	0.0497 (12)
C15	−0.6463 (6)	0.18141 (19)	0.6109 (4)	0.0615 (14)
C16	−0.5526 (6)	0.1420 (2)	0.5672 (5)	0.0935 (19)
H16A	−0.6243	0.1222	0.5018	0.140*
H16B	−0.4981	0.1190	0.6327	0.140*
H16C	−0.4752	0.1595	0.5389	0.140*
C17	−0.4031 (5)	0.22546 (18)	0.7553 (4)	0.0645 (15)
H17A	−0.3820	0.2618	0.7778	0.077*
H17B	−0.3447	0.2165	0.7005	0.077*
C18	−0.3436 (5)	0.19203 (18)	0.8684 (4)	0.0582 (13)
H18A	−0.4014	0.2013	0.9234	0.070*
H18B	−0.3664	0.1558	0.8459	0.070*
C19	−0.1661 (5)	0.19827 (19)	0.9332 (4)	0.0640 (14)
H19A	−0.1407	0.2351	0.9376	0.077*
H19B	−0.1423	0.1857	1.0158	0.077*
C20	−0.0576 (5)	0.17074 (18)	0.8769 (5)	0.0549 (13)
C21	0.1192 (5)	0.17729 (19)	0.9435 (4)	0.0640 (14)
H21A	0.1390	0.1687	1.0283	0.077*
H21B	0.1459	0.2138	0.9401	0.077*
C22	0.2331 (5)	0.14550 (19)	0.8985 (4)	0.0629 (14)
H22A	0.1977	0.1470	0.8104	0.075*
H22B	0.3391	0.1611	0.9286	0.075*
C23	0.2449 (5)	0.08920 (19)	0.9373 (4)	0.0656 (14)
H23A	0.2737	0.0873	1.0251	0.079*
H23B	0.1413	0.0725	0.9021	0.079*
N1	−0.8030 (5)	0.18326 (15)	0.5730 (3)	0.0632 (11)
N2	−0.5748 (4)	0.21841 (15)	0.6929 (3)	0.0551 (11)
N3	0.3650 (4)	0.06156 (15)	0.8987 (4)	0.0570 (11)
N4	0.4803 (5)	0.02109 (15)	0.7805 (4)	0.0659 (12)
O1	−0.1070 (3)	0.14430 (13)	0.7855 (3)	0.0654 (10)
O1W	0.5198 (5)	−0.06286 (16)	0.6451 (4)	0.1008 (14)
H1A	0.548 (7)	−0.0316 (14)	0.687 (4)	0.151*
H1B	0.455 (7)	−0.052 (2)	0.570 (3)	0.151*
O2W	0.2025 (6)	0.02126 (17)	0.3906 (5)	0.1258 (18)
H2A	0.308 (3)	0.028 (3)	0.425 (5)	0.189*
H2B	0.155 (7)	0.0522 (16)	0.366 (8)	0.189*
O3W	0.7904 (5)	0.08554 (17)	0.5440 (4)	0.0971 (13)
H3A	0.780 (8)	0.0512 (11)	0.559 (6)	0.146*
H3B	0.825 (8)	0.099 (3)	0.618 (3)	0.146*
O4W	0.2093 (7)	0.1308 (3)	0.2426 (5)	0.153 (2)
H4A	0.129 (7)	0.126 (4)	0.276 (8)	0.229*
H4B	0.289 (7)	0.109 (3)	0.289 (8)	0.229*
O5W	0.5163 (4)	0.39697 (15)	0.9246 (3)	0.0828 (12)
H5A	0.457 (6)	0.404 (3)	0.973 (5)	0.124*
H5B	0.576 (6)	0.3710 (17)	0.968 (5)	0.124*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.056 (3)	0.058 (4)	0.097 (4)	0.009 (3)	0.030 (3)	0.006 (3)
C2	0.054 (3)	0.047 (3)	0.069 (3)	0.003 (2)	0.025 (3)	0.004 (3)
C3	0.050 (3)	0.053 (3)	0.058 (3)	0.005 (2)	0.012 (3)	0.010 (3)
C4	0.067 (3)	0.058 (4)	0.071 (4)	0.008 (3)	0.015 (3)	−0.003 (3)
C5	0.066 (4)	0.078 (4)	0.082 (4)	−0.001 (3)	0.003 (3)	−0.004 (3)
C6	0.048 (3)	0.082 (4)	0.097 (5)	−0.002 (3)	0.010 (3)	0.004 (4)
C7	0.053 (3)	0.067 (4)	0.059 (3)	0.004 (3)	0.015 (3)	0.003 (3)
C8	0.063 (3)	0.108 (5)	0.086 (4)	0.009 (3)	0.005 (3)	−0.006 (3)
C9	0.050 (3)	0.050 (3)	0.055 (3)	−0.003 (2)	0.008 (2)	−0.001 (3)
C10	0.045 (3)	0.084 (4)	0.071 (3)	0.004 (3)	0.008 (3)	0.012 (3)
C11	0.065 (3)	0.076 (4)	0.084 (4)	0.022 (3)	0.026 (3)	0.007 (3)
C12	0.082 (4)	0.062 (4)	0.086 (4)	0.015 (3)	0.032 (3)	0.002 (3)
C13	0.064 (3)	0.057 (4)	0.070 (3)	−0.003 (3)	0.017 (3)	0.005 (3)
C14	0.050 (3)	0.042 (3)	0.056 (3)	0.006 (2)	0.015 (2)	0.000 (2)
C15	0.064 (3)	0.052 (4)	0.067 (3)	0.009 (3)	0.019 (3)	−0.004 (3)
C16	0.085 (4)	0.096 (5)	0.100 (4)	0.011 (3)	0.030 (3)	−0.026 (4)
C17	0.047 (3)	0.051 (3)	0.088 (4)	−0.001 (2)	0.013 (3)	0.002 (3)
C18	0.042 (3)	0.062 (3)	0.068 (3)	0.004 (2)	0.015 (2)	−0.003 (3)
C19	0.047 (3)	0.066 (4)	0.074 (3)	0.012 (2)	0.015 (3)	−0.008 (3)
C20	0.059 (3)	0.043 (3)	0.059 (3)	0.002 (2)	0.014 (3)	0.005 (3)
C21	0.044 (3)	0.062 (3)	0.078 (3)	0.006 (2)	0.010 (3)	0.000 (3)
C22	0.048 (3)	0.064 (4)	0.078 (4)	0.010 (2)	0.023 (3)	0.012 (3)
C23	0.052 (3)	0.067 (4)	0.080 (3)	0.015 (3)	0.023 (3)	0.015 (3)
N1	0.054 (2)	0.062 (3)	0.065 (3)	0.000 (2)	0.008 (2)	−0.012 (2)
N2	0.044 (2)	0.055 (3)	0.063 (3)	0.0036 (19)	0.012 (2)	−0.001 (2)
N3	0.046 (2)	0.063 (3)	0.061 (3)	0.0081 (19)	0.016 (2)	0.002 (2)
N4	0.059 (3)	0.065 (3)	0.070 (3)	0.001 (2)	0.017 (2)	−0.008 (2)
O1	0.057 (2)	0.070 (3)	0.066 (2)	0.0025 (17)	0.0161 (17)	−0.0130 (19)
O1W	0.073 (3)	0.117 (3)	0.113 (3)	0.002 (2)	0.031 (2)	−0.033 (3)
O2W	0.099 (3)	0.099 (4)	0.187 (5)	−0.008 (3)	0.057 (4)	−0.019 (3)
O3W	0.080 (3)	0.098 (3)	0.106 (3)	0.000 (3)	0.020 (2)	−0.023 (3)
O4W	0.135 (5)	0.180 (6)	0.129 (4)	−0.010 (4)	0.023 (4)	0.042 (4)
O5W	0.079 (3)	0.077 (3)	0.080 (3)	0.004 (2)	0.009 (2)	0.008 (2)

Geometric parameters (Å, º)

C1—C6	1.359 (7)	C16—H16B	0.9600
C1—C2	1.385 (6)	C16—H16C	0.9600
C1—H1	0.9300	C17—N2	1.460 (5)
C2—N4	1.382 (6)	C17—C18	1.513 (6)
C2—C3	1.400 (6)	C17—H17A	0.9700
C3—C4	1.376 (6)	C17—H17B	0.9700
C3—N3	1.392 (5)	C18—C19	1.507 (5)
C4—C5	1.376 (6)	C18—H18A	0.9700
C4—H4	0.9300	C18—H18B	0.9700

C5—C6	1.388 (7)	C19—C20	1.501 (6)
C5—H5	0.9300	C19—H19A	0.9700
C6—H6	0.9300	C19—H19B	0.9700
C7—N4	1.306 (6)	C20—O1	1.216 (5)
C7—N3	1.358 (6)	C20—C21	1.506 (6)
C7—C8	1.496 (5)	C21—C22	1.513 (6)
C8—H8A	0.9600	C21—H21A	0.9700
C8—H8B	0.9600	C21—H21B	0.9700
C8—H8C	0.9600	C22—C23	1.507 (6)
C9—N1	1.386 (4)	C22—H22A	0.9700
C9—C10	1.390 (3)	C22—H22B	0.9700
C9—C14	1.390 (3)	C23—N3	1.461 (5)
C10—C11	1.390 (3)	C23—H23A	0.9700
C10—H10	0.9300	C23—H23B	0.9700
C11—C12	1.390 (3)	O1W—H1A	0.93 (2)
C11—H11	0.9300	O1W—H1B	0.92 (4)
C12—C13	1.390 (3)	O2W—H2A	0.90 (2)
C12—H12	0.9300	O2W—H2B	0.90 (5)
C13—C14	1.390 (3)	O3W—H3A	0.91 (2)
C13—H13	0.9300	O3W—H3B	0.88 (5)
C14—N2	1.352 (4)	O4W—H4A	0.92 (7)
C15—N1	1.307 (6)	O4W—H4B	0.92 (8)
C15—N2	1.348 (6)	O5W—H5A	0.90 (6)
C15—C16	1.496 (7)	O5W—H5B	0.90 (5)
C16—H16A	0.9600		

C6—C1—C2	118.6 (5)	H16B—C16—H16C	109.5
C6—C1—H1	120.7	N2—C17—C18	111.8 (4)
C2—C1—H1	120.7	N2—C17—H17A	109.3
N4—C2—C1	132.0 (5)	C18—C17—H17A	109.3
N4—C2—C3	109.0 (4)	N2—C17—H17B	109.3
C1—C2—C3	119.0 (5)	C18—C17—H17B	109.3
C4—C3—N3	131.9 (5)	H17A—C17—H17B	107.9
C4—C3—C2	122.7 (4)	C19—C18—C17	112.6 (4)
N3—C3—C2	105.4 (4)	C19—C18—H18A	109.1
C3—C4—C5	116.6 (5)	C17—C18—H18A	109.1
C3—C4—H4	121.7	C19—C18—H18B	109.1
C5—C4—H4	121.7	C17—C18—H18B	109.1
C4—C5—C6	121.4 (5)	H18A—C18—H18B	107.8
C4—C5—H5	119.3	C20—C19—C18	115.9 (4)
C6—C5—H5	119.3	C20—C19—H19A	108.3
C1—C6—C5	121.6 (5)	C18—C19—H19A	108.3
C1—C6—H6	119.2	C20—C19—H19B	108.3
C5—C6—H6	119.2	C18—C19—H19B	108.3
N4—C7—N3	112.7 (4)	H19A—C19—H19B	107.4
N4—C7—C8	125.0 (4)	O1—C20—C19	123.2 (4)
N3—C7—C8	122.3 (4)	O1—C20—C21	121.8 (4)
C7—C8—H8A	109.5	C19—C20—C21	115.0 (4)

C7—C8—H8B	109.5	C20—C21—C22	117.0 (4)
H8A—C8—H8B	109.5	C20—C21—H21A	108.1
C7—C8—H8C	109.5	C22—C21—H21A	108.1
H8A—C8—H8C	109.5	C20—C21—H21B	108.1
H8B—C8—H8C	109.5	C22—C21—H21B	108.1
N1—C9—C10	131.51 (17)	H21A—C21—H21B	107.3
N1—C9—C14	108.49 (18)	C23—C22—C21	113.7 (4)
C10—C9—C14	119.99 (18)	C23—C22—H22A	108.8
C11—C10—C9	120.00 (18)	C21—C22—H22A	108.8
C11—C10—H10	120.0	C23—C22—H22B	108.8
C9—C10—H10	120.0	C21—C22—H22B	108.8
C12—C11—C10	120.00 (18)	H22A—C22—H22B	107.7
C12—C11—H11	120.0	N3—C23—C22	111.1 (4)
C10—C11—H11	120.0	N3—C23—H23A	109.4
C13—C12—C11	119.99 (18)	C22—C23—H23A	109.4
C13—C12—H12	120.0	N3—C23—H23B	109.4
C11—C12—H12	120.0	C22—C23—H23B	109.4
C14—C13—C12	120.00 (18)	H23A—C23—H23B	108.0
C14—C13—H13	120.0	C15—N1—C9	104.4 (3)
C12—C13—H13	120.0	C15—N2—C14	105.6 (3)
N2—C14—C13	132.77 (18)	C15—N2—C17	127.5 (4)
N2—C14—C9	107.23 (18)	C14—N2—C17	126.8 (4)
C13—C14—C9	120.01 (18)	C7—N3—C3	106.6 (4)
N1—C15—N2	114.3 (4)	C7—N3—C23	128.3 (4)
N1—C15—C16	123.4 (5)	C3—N3—C23	124.4 (4)
N2—C15—C16	122.3 (5)	C7—N4—C2	106.3 (4)
C15—C16—H16A	109.5	H1A—O1W—H1B	102 (3)
C15—C16—H16B	109.5	H2A—O2W—H2B	106 (4)
H16A—C16—H16B	109.5	H3A—O3W—H3B	103 (7)
C15—C16—H16C	109.5	H4A—O4W—H4B	102 (7)
H16A—C16—H16C	109.5	H5A—O5W—H5B	99 (6)

C6—C1—C2—N4	−179.8 (5)	C21—C22—C23—N3	−175.9 (4)
C6—C1—C2—C3	−0.1 (7)	N2—C15—N1—C9	−0.7 (5)
N4—C2—C3—C4	−179.8 (4)	C16—C15—N1—C9	179.7 (4)
C1—C2—C3—C4	0.5 (7)	C10—C9—N1—C15	−178.9 (2)
N4—C2—C3—N3	−0.7 (5)	C14—C9—N1—C15	0.2 (4)
C1—C2—C3—N3	179.5 (4)	N1—C15—N2—C14	0.8 (5)
N3—C3—C4—C5	−179.4 (5)	C16—C15—N2—C14	−179.6 (4)
C2—C3—C4—C5	−0.6 (7)	N1—C15—N2—C17	177.5 (4)
C3—C4—C5—C6	0.4 (8)	C16—C15—N2—C17	−2.9 (8)
C2—C1—C6—C5	−0.1 (8)	C13—C14—N2—C15	178.8 (2)
C4—C5—C6—C1	−0.1 (9)	C9—C14—N2—C15	−0.6 (3)
N1—C9—C10—C11	179.1 (2)	C13—C14—N2—C17	2.1 (5)
C14—C9—C10—C11	0.0	C9—C14—N2—C17	−177.3 (3)
C9—C10—C11—C12	0.0	C18—C17—N2—C15	−85.2 (6)
C10—C11—C12—C13	0.0	C18—C17—N2—C14	90.8 (5)
C11—C12—C13—C14	0.0	N4—C7—N3—C3	1.7 (5)

C12—C13—C14—N2	−179.4 (2)	C8—C7—N3—C3	−179.4 (4)
C12—C13—C14—C9	0.0	N4—C7—N3—C23	172.2 (4)
N1—C9—C14—N2	0.3 (2)	C8—C7—N3—C23	−8.9 (7)
C10—C9—C14—N2	179.52 (18)	C4—C3—N3—C7	178.4 (5)
N1—C9—C14—C13	−179.26 (19)	C2—C3—N3—C7	−0.5 (5)
C10—C9—C14—C13	0.0	C4—C3—N3—C23	7.4 (8)
N2—C17—C18—C19	179.3 (4)	C2—C3—N3—C23	−171.5 (4)
C17—C18—C19—C20	−76.8 (5)	C22—C23—N3—C7	−88.9 (6)
C18—C19—C20—O1	−0.8 (7)	C22—C23—N3—C3	80.1 (5)
C18—C19—C20—C21	−179.7 (4)	N3—C7—N4—C2	−2.1 (5)
O1—C20—C21—C22	−5.5 (7)	C8—C7—N4—C2	179.0 (4)
C19—C20—C21—C22	173.4 (4)	C1—C2—N4—C7	−178.6 (5)
C20—C21—C22—C23	−77.5 (5)	C3—C2—N4—C7	1.7 (5)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*W*—H1*A*···N4	0.93 (2)	1.95 (4)	2.758 (6)	144 (5)
O1*W*—H1*B*···O3*W*^{i}	0.92 (4)	2.31 (5)	2.954 (5)	127 (5)
O2*W*—H2*B*···O4*W*	0.90 (5)	2.61 (6)	3.308 (7)	135 (7)
O2*W*—H2*B*···O5*W*^{ii}	0.90 (5)	2.05 (7)	2.770 (6)	136 (8)
O3*W*—H3*B*···O1^{iii}	0.88 (5)	2.18 (5)	3.054 (6)	171 (7)
O4*W*—H4*B*···O1*W*^{i}	0.92 (8)	2.00 (7)	2.900 (7)	166 (8)
O4*W*—H4*A*···O5*W*^{ii}	0.92 (7)	2.33 (4)	3.200 (7)	157 (7)
O5*W*—H5*B*···N1^{iv}	0.90 (5)	1.93 (5)	2.822 (5)	175 (6)
O5*W*—H5*A*···O3*W*^{v}	0.90 (6)	1.92 (6)	2.811 (6)	167 (6)
O3*W*—H3*A*···O2*W*^{i}	0.91 (2)	1.94 (2)	2.840 (7)	170 (6)
O2*W*—H2*A*···O1*W*^{i}	0.90 (2)	2.14 (5)	2.823 (6)	132 (5)

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