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Dihydrocyclam dimaleate [H₂(cyclam)(maleate)₂]

Mbonzi Ombenga Mireille Ninon,^a Mohammed Fahim,^a
 Mohammed Lachkar,^{b*} José Luis Marco Contelles,^c
 Josefina Perles^d and Brahim El Bali^e

^aLCMSN, Département de Chimie, Faculté des Sciences, Université Moulay Ismail, BP 11201, 50000 Meknès, Morocco, ^bLIMOM (CNRST, URAC 19), Department of Chemistry, Faculty of Sciences, University Sidi Mohamed Ben Abdellah, BP 1796, 30000 Fès, Morocco, ^cLaboratorio de Radicales Libres y Química Computacional, Instituto de Química Orgánica General, Consejo Superior de Investigaciones Científicas, C/ Juan de la Cierva, 3, 28006-Madrid, Spain, ^dLaboratorio de Difracción de Rayos X de Monocristal, Servicio Interdepartamental de Investigación, Universidad Autónoma de Madrid, and ^eLCSMA, Department of Chemistry, Faculty of Sciences, University Mohamed I, P.O. Box 717, 60000 Oujda, Morocco
 Correspondence e-mail: limomusmba@gmail.com

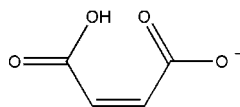
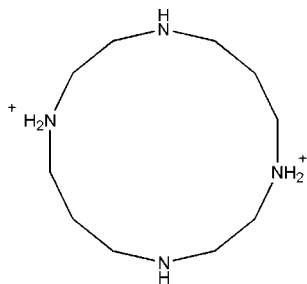
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Key indicators: single-crystal X-ray study; $T = 100$ K; mean $\sigma(\text{C}-\text{C}) = 0.002$ Å;
 R factor = 0.032; wR factor = 0.083; data-to-parameter ratio = 10.0.

The asymmetric unit of the title molecular salt [systematic name: 1,4,8,11-tetraazacyclotetradecane-1,8-dium bis(3-carboxyprop-2-enoate)], C₁₀H₂₆N₄²⁺·2C₄H₃O₄⁻, contains two half-cations (both completed by crystallographic inversion symmetry) and two maleate anions. The cyclam macrocycles adopt *trans*-III conformations, supported by two intramolecular N—H···O hydrogen bonds. The O-bonded H atom of each maleate ion is disordered over two positions with an occupancy ratio of 0.61 (5):0.39 (5): each one generates an intramolecular O—H···O hydrogen bond. In the crystal, the cations are linked to the anions by N—H···O hydrogen bonds, generating [001] chains.

Related literature

For related cyclam crystal structures, see: Robinson *et al.* (1989); Frémond *et al.* (2000); Meyer *et al.* (1998). For macrocycle conformations, see: Bosnich *et al.* (1965); Dale (1973, 1976); Melson (1979); Bandoli *et al.* (1993); Hancock *et al.* (1996).



Experimental

Crystal data

C₁₀H₂₆N₄²⁺·2C₄H₃O₄⁻
 $M_r = 432.48$
 Monoclinic, $P2_1/n$
 $a = 8.2925$ (1) Å
 $b = 13.5841$ (2) Å
 $c = 19.2995$ (3) Å
 $\beta = 98.797$ (1)°

$V = 2148.44$ (5) Å³
 $Z = 4$
 Cu $K\alpha$ radiation
 $\mu = 0.89$ mm⁻¹
 $T = 100$ K
 $0.25 \times 0.20 \times 0.20$ mm

Data collection

Bruker SMART CCD
 diffractometer
 Absorption correction: multi-scan
 (SADABS; Bruker, 2005)
 $T_{\min} = 0.81$, $T_{\max} = 0.84$

18854 measured reflections
 4018 independent reflections
 3821 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.024$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.032$
 $wR(F^2) = 0.083$
 $S = 1.04$
 4018 reflections
 403 parameters

H atoms treated by a mixture of
 independent and constrained
 refinement
 $\Delta\rho_{\text{max}} = 0.36$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.18$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1A···O2 ⁱ	0.920 (17)	1.800 (17)	2.7074 (13)	168.1 (14)
N1—H1B···N2	0.925 (16)	2.015 (15)	2.8000 (13)	141.7 (13)
N2—H2A···O7 ⁱⁱ	0.926 (16)	2.356 (16)	3.2134 (13)	153.9 (13)
N2—H2A···O8 ⁱⁱ	0.926 (16)	2.379 (16)	3.2178 (14)	150.6 (13)
N3—H3A···N4 ⁱⁱⁱ	0.899 (16)	2.089 (16)	2.8046 (14)	135.8 (13)
N3—H3B···O5 ^{iv}	0.901 (16)	2.397 (16)	3.0713 (13)	131.7 (12)
N3—H3B···O6 ^{iv}	0.901 (16)	2.037 (16)	2.8982 (13)	159.5 (14)
N4—H4···O4 ^v	0.868 (16)	2.348 (16)	3.1596 (12)	155.8 (13)
O3—H3O···O1	0.90 (3)	1.55 (3)	2.4444 (12)	178 (2)
O7—H7O···O5	0.92 (4)	1.50 (4)	2.4157 (13)	176 (3)

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

Data collection: SMART (Bruker, 2005); cell refinement: SAINT (Bruker, 2005); 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: SHELXL97.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB7135).

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supporting information

Acta Cryst. (2013). E69, o1574–o1575 [doi:10.1107/S1600536813025580]

Dihydrocyclam dimaleate [H₂(cyclam)(maleate)₂]

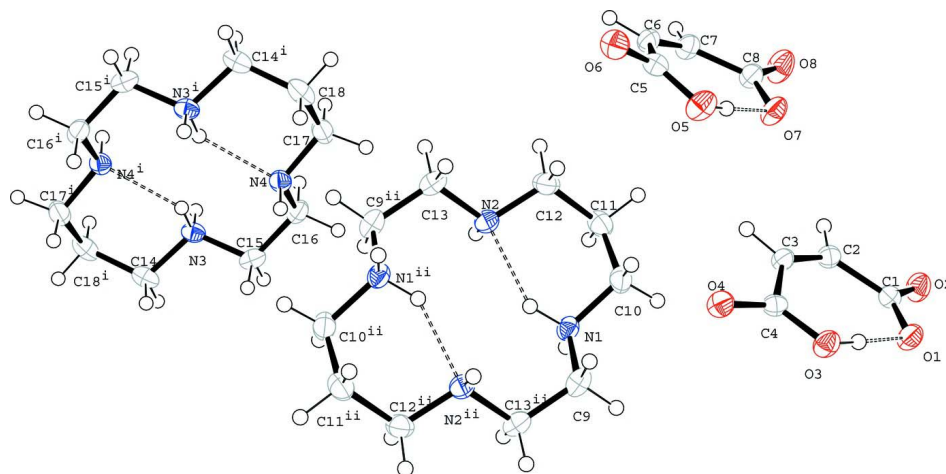
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S1. Comment

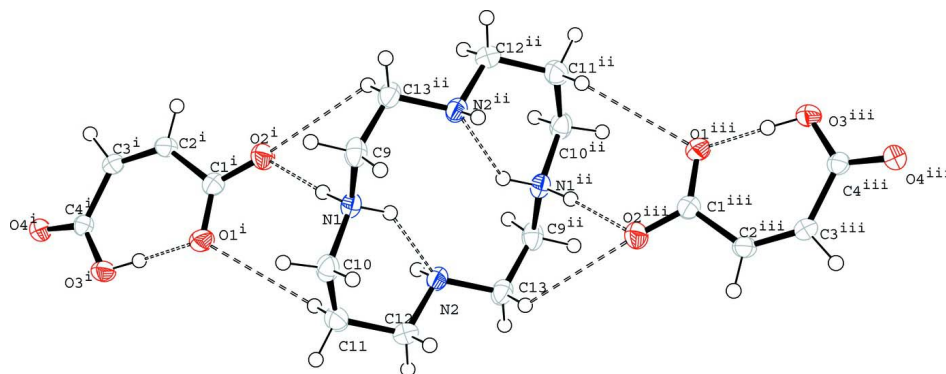
Cyclam is doubly protonated in [H₂(cyclam)(maleate)₂], resulting in a maleate monoanion. The di-protonated cyclam [C₁₀H₂₆N₄]²⁺ exhibits bond distances and angles in the range usually found in the literature (Melson, 1979). The two additional protons on N1 and N1A are *trans* to each other and interact through hydrogen bonds with the nonprotonated N2 and N2A nitrogen atoms [N1⋯N2= 2.800 (1) Å, N3⋯N4= 2.805 (1) Å]. The diprotonated macrocycle adopts an quadrangular (3,4,3,4)-C conformation (Fig. 1) according to Dale's nomenclature [(Dale, 1973 and 1976, (Hancock *et al.*, 1996)], where the *exo*-cyclic nitrogen atom N2 is located two bonds away from the adjacent corner atoms C9A and C11, while the amine nitrogen atom N1A is located one bond away from the corresponding corner atom C9A and two bonds away from C11A. According to the stereochemical classification of 1,4,8,11 tetraazacyclotetradecane introduced by Bosnich *et al.* (1965), the cyclam ring adopts a *trans*-III geometry type, which, according to molecular mechanics *MM*-calculations, is the most stable among the five possible configurations (Bandoli *et al.*, 1993). In the crystal structure, intramolecular hydrogen bonds occur, linking carboxylate O atoms in each maleate ion. The H3C and H7A atoms are involved in these bonds and maintain the charge balance by bridging two carboxylate groups within the structure. The complex features intra and intermolecular hydrogen bonds involving N—H⋯O, N—H⋯N and O—H⋯O. The main types of such bonds are those between protonated NH groups of the macrocycle and O atoms of the ionized maleic hydroxyls, between protonated and nonprotonated NH groups of the macrocycle and between O-atoms of the same ionized maleic hydroxyls as shown on Fig. 2 and 3. The values of the main H-bonds are reported in table 3.

S2. Experimental

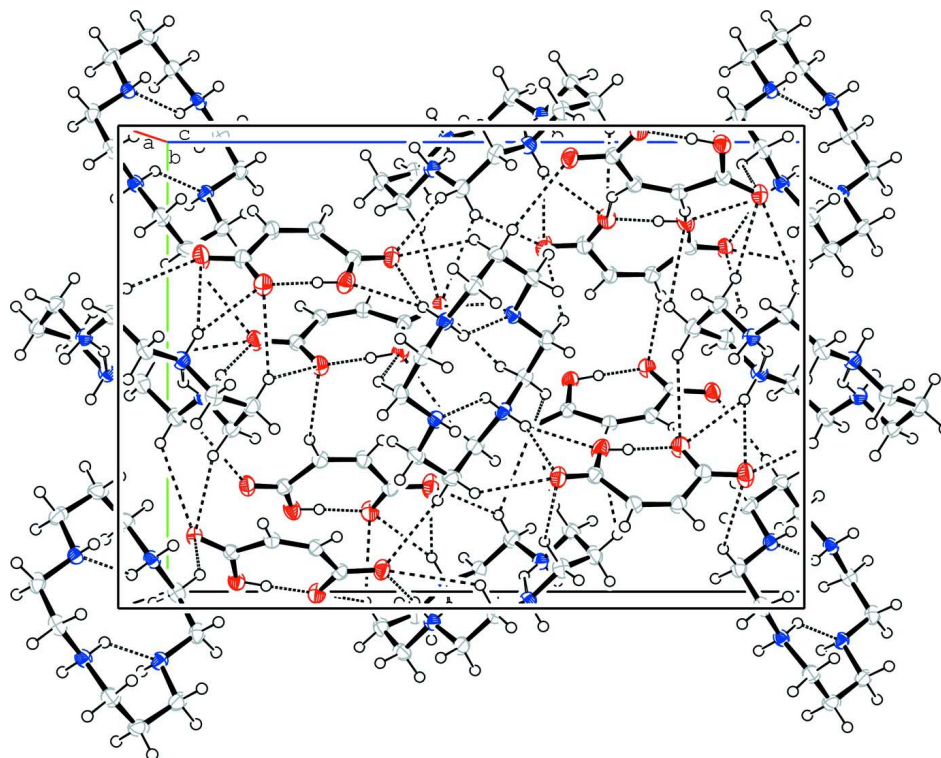
0.2 g (1 mmol) of cyclam C₁₀H₂₄N₄ was dissolved 25 ml of water-ethanol mixture 1:1 (v/v) and 0.233 g (2 mmol) of maleic acid C₄H₄O₄, in 25 ml of the same solvent. The solutions were combined, and the mixture was refluxed for 3 h, before to be deposited to set at room conditions. Prismatic coloureless crystals were obtained which were washed with a water (80%) /ethanol (20%) (v:v) solution.

**Figure 1**

The molecular structure of the title compound, with hydrogen bonds shown as dashed lines. Anisotropic displacement parameters drawn at the 50% probability level.

**Figure 2**

Inter-molecular H-bonds between cyclam and maleate ion.

**Figure 3**

Projection of the structure in *bc*-plane, hydrogen bonds as dashed lines.

1,4,8,11-Tetraazacyclotetradecane-1,8-dium bis(3-carboxyprop-2-enoate)

Crystal data

$C_{10}H_{26}N_4^{2+} \cdot 2C_4H_3O_4^-$

$M_r = 432.48$

Monoclinic, $P2_1/n$

$a = 8.2925$ (1) Å

$b = 13.5841$ (2) Å

$c = 19.2995$ (3) Å

$\beta = 98.797$ (1)°

$V = 2148.44$ (5) Å³

$Z = 4$

$F(000) = 928$

$D_x = 1.337$ Mg m⁻³

Cu $K\alpha$ radiation, $\lambda = 1.54178$ Å

$\mu = 0.89$ mm⁻¹

$T = 100$ K

Prism, colourless

$0.25 \times 0.20 \times 0.20$ mm

Data collection

Bruker SMART CCD
diffractometer

ω scans

Absorption correction: multi-scan
(*SADABS*; Bruker, 2005)

$T_{\min} = 0.81$, $T_{\max} = 0.84$

18854 measured reflections

4018 independent reflections

3821 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.024$

$\theta_{\max} = 70.1^\circ$, $\theta_{\min} = 4.6^\circ$

$h = -10 \rightarrow 9$

$k = -16 \rightarrow 16$

$l = -23 \rightarrow 23$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.032$
 $wR(F^2) = 0.083$
 $S = 1.04$
 4018 reflections
 403 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 atoms treated by a mixture of independent
 and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0406P)^2 + 0.6721P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.36 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.18 \text{ e } \text{\AA}^{-3}$

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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
C1	0.29130 (13)	0.94686 (8)	0.28537 (6)	0.0241 (2)	
C2	0.42219 (13)	0.89074 (8)	0.25661 (6)	0.0240 (2)	
C3	0.44193 (13)	0.87391 (8)	0.19031 (6)	0.0229 (2)	
C4	0.34069 (12)	0.90322 (8)	0.12233 (6)	0.0227 (2)	
C5	0.98341 (14)	0.76765 (8)	0.18188 (6)	0.0260 (2)	
C6	1.05748 (14)	0.70568 (9)	0.24264 (6)	0.0259 (2)	
C7	1.02908 (14)	0.70577 (9)	0.30874 (6)	0.0274 (2)	
C8	0.92026 (14)	0.76946 (9)	0.34489 (6)	0.0284 (2)	
C9	0.25226 (15)	0.61005 (9)	0.03030 (6)	0.0301 (3)	
C10	0.47726 (15)	0.63339 (9)	0.13169 (7)	0.0303 (3)	
C11	0.62753 (15)	0.58461 (10)	0.17098 (6)	0.0319 (3)	
C12	0.75542 (14)	0.55991 (10)	0.12458 (7)	0.0309 (3)	
C13	0.81528 (14)	0.46284 (9)	0.02577 (6)	0.0289 (3)	
C14	0.75571 (15)	-0.17204 (9)	-0.00831 (7)	0.0313 (3)	
C15	0.74127 (14)	-0.02422 (9)	0.06666 (6)	0.0283 (2)	
C16	0.84068 (14)	0.05815 (9)	0.10416 (6)	0.0281 (2)	
C17	1.02932 (15)	0.19107 (9)	0.08931 (6)	0.0306 (3)	
C18	1.12976 (16)	0.24033 (9)	0.03941 (7)	0.0335 (3)	
N1	0.38474 (12)	0.56356 (7)	0.08060 (5)	0.0245 (2)	
N2	0.69367 (11)	0.48659 (7)	0.07078 (5)	0.0258 (2)	
N3	0.84805 (11)	-0.09675 (7)	0.03828 (5)	0.0243 (2)	
N4	0.92438 (12)	0.11249 (7)	0.05474 (5)	0.0248 (2)	
O1	0.18816 (10)	0.99727 (6)	0.24442 (4)	0.03003 (19)	
H1O	0.2061	0.9906	0.203	0.045*	0.39 (5)

O2	0.29456 (10)	0.94215 (6)	0.35007 (4)	0.0326 (2)	
O3	0.22552 (10)	0.96878 (6)	0.12282 (4)	0.02853 (19)	
O4	0.37276 (9)	0.86677 (6)	0.06808 (4)	0.02820 (19)	
O5	0.85713 (11)	0.82014 (7)	0.18682 (5)	0.0352 (2)	
H5O	0.8402	0.8206	0.2286	0.053*	0.41 (5)
O6	1.04578 (11)	0.76384 (7)	0.12791 (4)	0.0332 (2)	
O7	0.81387 (10)	0.82564 (7)	0.30773 (5)	0.0340 (2)	
O8	0.93463 (12)	0.76651 (8)	0.40874 (5)	0.0430 (2)	
H1A	0.3368 (19)	0.5175 (12)	0.1059 (8)	0.036 (4)*	
H1B	0.4603 (19)	0.5331 (11)	0.0571 (8)	0.034 (4)*	
H2	0.4994 (17)	0.8649 (10)	0.2919 (7)	0.026 (3)*	
H2A	0.6715 (18)	0.4294 (12)	0.0937 (8)	0.035 (4)*	
H3	0.5346 (17)	0.8353 (10)	0.1825 (7)	0.026 (3)*	
H3A	0.9173 (18)	−0.0670 (11)	0.0134 (8)	0.032 (4)*	
H3B	0.9109 (19)	−0.1278 (11)	0.0739 (8)	0.034 (4)*	
H3O	0.211 (3)	0.9802 (17)	0.1673 (15)	0.023 (8)*	0.61 (5)
H4	0.8494 (19)	0.1373 (11)	0.0233 (8)	0.033 (4)*	
H6	1.1379 (17)	0.6605 (11)	0.2304 (8)	0.031 (3)*	
H7	1.0899 (18)	0.6622 (12)	0.3405 (8)	0.035 (4)*	
H7O	0.829 (3)	0.826 (2)	0.2615 (19)	0.033 (10)*	0.59 (5)
H9A	0.3008 (18)	0.6660 (12)	0.0107 (8)	0.036 (4)*	
H9B	0.1683 (17)	0.6323 (11)	0.0580 (8)	0.031 (3)*	
H10A	0.5089 (18)	0.6906 (11)	0.1055 (8)	0.033 (4)*	
H10B	0.4040 (17)	0.6548 (11)	0.1624 (8)	0.031 (3)*	
H11A	0.6791 (19)	0.6312 (12)	0.2085 (8)	0.039 (4)*	
H11B	0.5941 (17)	0.5260 (11)	0.1945 (8)	0.031 (3)*	
H12A	0.7842 (17)	0.6192 (11)	0.0991 (7)	0.030 (3)*	
H12B	0.855 (2)	0.5371 (11)	0.1536 (8)	0.038 (4)*	
H13A	0.8453 (17)	0.5260 (11)	0.0028 (7)	0.028 (3)*	
H13B	0.9123 (19)	0.4366 (11)	0.0525 (8)	0.033 (4)*	
H14A	0.6835 (18)	−0.1343 (11)	−0.0437 (8)	0.034 (4)*	
H14B	0.6853 (19)	−0.2065 (12)	0.0195 (8)	0.039 (4)*	
H15A	0.6656 (17)	0.0007 (10)	0.0272 (7)	0.025 (3)*	
H15B	0.6817 (18)	−0.0594 (11)	0.0973 (8)	0.034 (4)*	
H16A	0.9219 (17)	0.0315 (10)	0.1411 (7)	0.028 (3)*	
H16B	0.7675 (18)	0.1014 (11)	0.1274 (8)	0.033 (4)*	
H17A	1.1036 (17)	0.1611 (10)	0.1290 (7)	0.028 (3)*	
H17B	0.9618 (18)	0.2419 (12)	0.1109 (8)	0.036 (4)*	
H18A	1.0582 (19)	0.2722 (11)	0.0018 (8)	0.036 (4)*	
H18B	1.1958 (19)	0.2909 (12)	0.0640 (8)	0.039 (4)*	

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0230 (5)	0.0242 (5)	0.0252 (5)	−0.0015 (4)	0.0038 (4)	−0.0028 (4)
C2	0.0228 (5)	0.0247 (5)	0.0235 (5)	0.0025 (4)	0.0007 (4)	0.0005 (4)
C3	0.0196 (5)	0.0231 (5)	0.0261 (5)	0.0023 (4)	0.0034 (4)	0.0001 (4)
C4	0.0201 (5)	0.0239 (5)	0.0243 (5)	−0.0021 (4)	0.0040 (4)	0.0022 (4)

C5	0.0261 (5)	0.0270 (5)	0.0238 (5)	-0.0043 (4)	0.0005 (4)	0.0003 (4)
C6	0.0235 (5)	0.0275 (6)	0.0261 (6)	0.0040 (4)	0.0025 (4)	-0.0013 (4)
C7	0.0267 (6)	0.0300 (6)	0.0245 (5)	0.0073 (5)	0.0006 (4)	0.0031 (5)
C8	0.0265 (6)	0.0319 (6)	0.0270 (6)	0.0035 (5)	0.0046 (4)	-0.0003 (5)
C9	0.0322 (6)	0.0314 (6)	0.0286 (6)	0.0088 (5)	0.0108 (5)	0.0045 (5)
C10	0.0332 (6)	0.0265 (6)	0.0337 (6)	-0.0034 (5)	0.0133 (5)	-0.0063 (5)
C11	0.0350 (6)	0.0339 (6)	0.0273 (6)	-0.0077 (5)	0.0066 (5)	-0.0046 (5)
C12	0.0243 (6)	0.0366 (6)	0.0312 (6)	-0.0054 (5)	0.0029 (5)	-0.0024 (5)
C13	0.0234 (5)	0.0362 (6)	0.0283 (6)	0.0052 (5)	0.0072 (5)	0.0056 (5)
C14	0.0302 (6)	0.0323 (6)	0.0291 (6)	-0.0103 (5)	-0.0024 (5)	0.0020 (5)
C15	0.0209 (5)	0.0360 (6)	0.0283 (6)	0.0020 (5)	0.0051 (4)	0.0075 (5)
C16	0.0259 (6)	0.0359 (6)	0.0230 (5)	0.0077 (5)	0.0056 (4)	-0.0002 (5)
C17	0.0331 (6)	0.0273 (6)	0.0290 (6)	0.0034 (5)	-0.0030 (5)	-0.0068 (5)
C18	0.0398 (7)	0.0236 (6)	0.0328 (6)	-0.0046 (5)	-0.0083 (5)	-0.0007 (5)
N1	0.0243 (5)	0.0245 (5)	0.0265 (5)	0.0006 (4)	0.0098 (4)	-0.0007 (4)
N2	0.0234 (5)	0.0284 (5)	0.0268 (5)	-0.0021 (4)	0.0082 (4)	0.0003 (4)
N3	0.0224 (5)	0.0269 (5)	0.0229 (5)	-0.0033 (4)	0.0007 (4)	0.0039 (4)
N4	0.0246 (5)	0.0258 (5)	0.0227 (5)	0.0031 (4)	-0.0009 (4)	-0.0007 (4)
O1	0.0262 (4)	0.0355 (4)	0.0282 (4)	0.0088 (3)	0.0038 (3)	-0.0013 (4)
O2	0.0365 (5)	0.0374 (5)	0.0247 (4)	0.0074 (4)	0.0076 (3)	-0.0025 (3)
O3	0.0278 (4)	0.0313 (4)	0.0257 (4)	0.0082 (3)	0.0017 (3)	0.0031 (3)
O4	0.0275 (4)	0.0357 (4)	0.0216 (4)	0.0025 (3)	0.0045 (3)	0.0008 (3)
O5	0.0337 (5)	0.0425 (5)	0.0286 (5)	0.0118 (4)	0.0026 (3)	0.0092 (4)
O6	0.0375 (5)	0.0395 (5)	0.0232 (4)	-0.0024 (4)	0.0064 (3)	0.0016 (3)
O7	0.0311 (4)	0.0404 (5)	0.0306 (5)	0.0142 (4)	0.0053 (3)	0.0018 (4)
O8	0.0473 (5)	0.0572 (6)	0.0254 (4)	0.0175 (5)	0.0083 (4)	-0.0004 (4)

Geometric parameters (Å, °)

C1—O2	1.2463 (14)	C13—N2	1.4641 (14)
C1—O1	1.2722 (14)	C13—C9 ⁱ	1.5099 (18)
C1—C2	1.5007 (15)	C13—H13A	1.014 (15)
C2—C3	1.3343 (16)	C13—H13B	0.956 (16)
C2—H2	0.930 (14)	C14—N3	1.4933 (15)
C3—C4	1.4991 (15)	C14—C18 ⁱⁱ	1.5156 (19)
C3—H3	0.961 (14)	C14—H14A	0.981 (16)
C4—O4	1.2236 (14)	C14—H14B	0.972 (16)
C4—O3	1.3070 (14)	C15—N3	1.4843 (15)
C5—O6	1.2328 (14)	C15—C16	1.5076 (17)
C5—O5	1.2824 (15)	C15—H15A	0.971 (14)
C5—C6	1.4969 (16)	C15—H15B	0.954 (16)
C6—C7	1.3321 (17)	C16—N4	1.4625 (15)
C6—H6	0.962 (15)	C16—H16A	0.973 (14)
C7—C8	1.4975 (16)	C16—H16B	0.998 (15)
C7—H7	0.941 (16)	C17—N4	1.4712 (15)
C8—O8	1.2204 (15)	C17—C18	1.5213 (19)
C8—O7	1.2967 (15)	C17—H17A	0.994 (14)
C9—N1	1.4906 (15)	C17—H17B	1.017 (16)

C9—C13 ⁱ	1.5099 (18)	C18—C14 ⁱⁱ	1.5155 (19)
C9—H9A	0.963 (16)	C18—H18A	0.967 (16)
C9—H9B	0.988 (15)	C18—H18B	0.958 (17)
C10—N1	1.4929 (15)	N1—H1A	0.920 (17)
C10—C11	1.5093 (18)	N1—H1B	0.925 (16)
C10—H10A	0.984 (16)	N2—H2A	0.926 (16)
C10—H10B	0.956 (15)	N3—H3A	0.899 (16)
C11—C12	1.5262 (17)	N3—H3B	0.901 (16)
C11—H11A	1.007 (16)	N4—H4	0.868 (16)
C11—H11B	0.978 (15)	O1—H1O	0.84
C12—N2	1.4729 (16)	O3—H3O	0.90 (3)
C12—H12A	0.992 (15)	O5—H5O	0.84
C12—H12B	0.977 (16)	O7—H7O	0.92 (4)
O2—C1—O1	124.03 (10)	H13A—C13—H13B	108.0 (12)
O2—C1—C2	116.00 (10)	N3—C14—C18 ⁱⁱ	111.28 (10)
O1—C1—C2	119.95 (10)	N3—C14—H14A	105.3 (9)
C3—C2—C1	130.06 (10)	C18 ⁱⁱ —C14—H14A	113.4 (9)
C3—C2—H2	117.8 (8)	N3—C14—H14B	107.1 (9)
C1—C2—H2	112.1 (8)	C18 ⁱⁱ —C14—H14B	112.9 (9)
C2—C3—C4	131.25 (10)	H14A—C14—H14B	106.4 (12)
C2—C3—H3	117.6 (8)	N3—C15—C16	110.89 (9)
C4—C3—H3	111.2 (8)	N3—C15—H15A	107.0 (8)
O4—C4—O3	122.45 (10)	C16—C15—H15A	111.0 (8)
O4—C4—C3	118.39 (10)	N3—C15—H15B	106.9 (9)
O3—C4—C3	119.12 (9)	C16—C15—H15B	111.8 (9)
O6—C5—O5	122.62 (11)	H15A—C15—H15B	109.1 (12)
O6—C5—C6	117.60 (10)	N4—C16—C15	109.92 (9)
O5—C5—C6	119.75 (10)	N4—C16—H16A	108.8 (8)
C7—C6—C5	129.66 (11)	C15—C16—H16A	110.0 (8)
C7—C6—H6	117.9 (9)	N4—C16—H16B	112.1 (8)
C5—C6—H6	112.5 (9)	C15—C16—H16B	109.1 (8)
C6—C7—C8	130.85 (11)	H16A—C16—H16B	106.9 (12)
C6—C7—H7	117.9 (9)	N4—C17—C18	112.03 (10)
C8—C7—H7	111.1 (9)	N4—C17—H17A	107.8 (8)
O8—C8—O7	122.06 (11)	C18—C17—H17A	109.5 (8)
O8—C8—C7	118.61 (11)	N4—C17—H17B	110.8 (8)
O7—C8—C7	119.33 (10)	C18—C17—H17B	110.4 (9)
N1—C9—C13 ⁱ	110.16 (9)	H17A—C17—H17B	106.1 (12)
N1—C9—H9A	106.2 (9)	C14 ⁱⁱ —C18—C17	114.74 (10)
C13 ⁱ —C9—H9A	111.6 (9)	C14 ⁱⁱ —C18—H18A	109.1 (9)
N1—C9—H9B	106.7 (8)	C17—C18—H18A	109.9 (9)
C13 ⁱ —C9—H9B	111.9 (8)	C14 ⁱⁱ —C18—H18B	106.9 (9)
H9A—C9—H9B	110.0 (12)	C17—C18—H18B	109.1 (9)
N1—C10—C11	110.75 (10)	H18A—C18—H18B	106.8 (13)
N1—C10—H10A	108.3 (9)	C9—N1—C10	114.46 (9)
C11—C10—H10A	109.9 (9)	C9—N1—H1A	107.3 (10)
N1—C10—H10B	106.9 (9)	C10—N1—H1A	107.6 (10)

C11—C10—H10B	112.1 (9)	C9—N1—H1B	110.9 (9)
H10A—C10—H10B	108.7 (12)	C10—N1—H1B	106.8 (9)
C10—C11—C12	113.34 (10)	H1A—N1—H1B	109.6 (13)
C10—C11—H11A	108.2 (9)	C13—N2—C12	111.75 (9)
C12—C11—H11A	107.7 (9)	C13—N2—H2A	107.7 (9)
C10—C11—H11B	108.7 (8)	C12—N2—H2A	107.7 (9)
C12—C11—H11B	111.5 (8)	C15—N3—C14	113.39 (9)
H11A—C11—H11B	107.3 (12)	C15—N3—H3A	111.3 (9)
N2—C12—C11	111.37 (10)	C14—N3—H3A	107.3 (9)
N2—C12—H12A	106.5 (8)	C15—N3—H3B	109.7 (10)
C11—C12—H12A	110.7 (8)	C14—N3—H3B	108.8 (10)
N2—C12—H12B	111.2 (9)	H3A—N3—H3B	106.0 (13)
C11—C12—H12B	109.8 (9)	C16—N4—C17	112.16 (9)
H12A—C12—H12B	107.1 (12)	C16—N4—H4	106.9 (10)
N2—C13—C9 ⁱ	110.86 (10)	C17—N4—H4	110.3 (10)
N2—C13—H13A	108.1 (8)	C1—O1—H1O	109.5
C9 ⁱ —C13—H13A	109.3 (8)	C4—O3—H3O	109.3 (14)
N2—C13—H13B	111.2 (9)	C5—O5—H5O	109.5
C9 ⁱ —C13—H13B	109.4 (9)	C8—O7—H7O	111.2 (16)
O2—C1—C2—C3	172.92 (12)	C10—C11—C12—N2	-64.14 (14)
O1—C1—C2—C3	-8.76 (18)	N3—C15—C16—N4	63.16 (12)
C1—C2—C3—C4	-1.1 (2)	N4—C17—C18—C14 ⁱⁱ	-60.25 (13)
C2—C3—C4—O4	-169.79 (12)	C13 ⁱ —C9—N1—C10	171.04 (9)
C2—C3—C4—O3	12.43 (18)	C11—C10—N1—C9	-169.21 (10)
O6—C5—C6—C7	169.97 (12)	C9 ⁱ —C13—N2—C12	-178.28 (10)
O5—C5—C6—C7	-11.73 (19)	C11—C12—N2—C13	179.69 (10)
C5—C6—C7—C8	-2.7 (2)	C16—C15—N3—C14	-171.53 (10)
C6—C7—C8—O8	-167.94 (13)	C18 ⁱⁱ —C14—N3—C15	176.49 (10)
C6—C7—C8—O7	12.2 (2)	C15—C16—N4—C17	-177.39 (9)
N1—C10—C11—C12	67.08 (13)	C18—C17—N4—C16	173.98 (10)

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

Hydrogen-bond geometry (\AA , $^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1A \cdots O2 ⁱⁱⁱ	0.920 (17)	1.800 (17)	2.7074 (13)	168.1 (14)
N1—H1B \cdots N2	0.925 (16)	2.015 (15)	2.8000 (13)	141.7 (13)
N2—H2A \cdots O7 ^{iv}	0.926 (16)	2.356 (16)	3.2134 (13)	153.9 (13)
N2—H2A \cdots O8 ^{iv}	0.926 (16)	2.379 (16)	3.2178 (14)	150.6 (13)
N3—H3A \cdots N4 ⁱⁱ	0.899 (16)	2.089 (16)	2.8046 (14)	135.8 (13)
N3—H3B \cdots O5 ^v	0.901 (16)	2.397 (16)	3.0713 (13)	131.7 (12)
N3—H3B \cdots O6 ^v	0.901 (16)	2.037 (16)	2.8982 (13)	159.5 (14)
N4—H4 \cdots O4 ⁱ	0.868 (16)	2.348 (16)	3.1596 (12)	155.8 (13)
O3—H3O \cdots O1	0.90 (3)	1.55 (3)	2.4444 (12)	178 (2)
O7—H7O \cdots O5	0.92 (4)	1.50 (4)	2.4157 (13)	176 (3)

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