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4-(2,3-Dimethylphenyl)piperazin-1-ium chloride monohydrate

 Imen Ben Gharbia,^a Riadh Kefi,^a Meher El Glaoui,^a
 Erwann Jeanneau^b and Cherif Ben Nasr^{a*}
^aLaboratoire de Chimie des Matériaux, Faculté des Sciences de Bizerte, 7021 Zarzouna, Tunisia, and ^bUniversité Lyon1, Centre de Diffractométrie Henri Longchambon, 43 boulevard du 11 Novembre 1918, 69622 Villeurbanne Cedex, France

Correspondence e-mail: cherif_bennasr@yahoo.fr

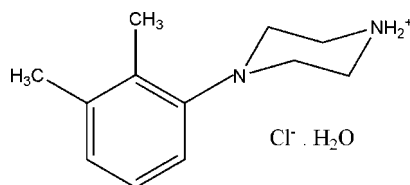
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 Key indicators: single-crystal X-ray study; $T = 150$ K; mean $\sigma(\text{C}-\text{C}) = 0.002$ Å; R factor = 0.036; wR factor = 0.036; data-to-parameter ratio = 17.2.

The title compound, $\text{C}_{12}\text{H}_{19}\text{N}_2^+\cdot\text{Cl}^-\cdot\text{H}_2\text{O}$, contains a network of 4-(2,3-dimethylphenyl)piperazin-1-ium cations, water molecules and chloride anions. The crystal packing is influenced by $\text{O}-\text{H}\cdots\text{Cl}$, $\text{N}-\text{H}\cdots\text{Cl}$, $\text{N}-\text{H}\cdots\text{O}$, $\text{C}-\text{H}\cdots\text{O}$ and $\text{C}-\text{H}\cdots\text{Cl}$ hydrogen bonds, resulting in structure with an open-framework architecture.

Related literature

For related literature, see: Ben Gharbia *et al.* (2005, 2007); Bernstein *et al.* (1995); Pajewski *et al.* (2004); Sessler *et al.* (2003); Schmidtchen & Berge (1997). For the refinement weighting scheme, see: Prince (1982); Watkin (1994).



Experimental

Crystal data

 $\text{C}_{12}\text{H}_{19}\text{N}_2^+\cdot\text{Cl}^-\cdot\text{H}_2\text{O}$
 $M_r = 244.76$

 Triclinic, $P\bar{1}$
 $a = 7.5439$ (3) Å

 $b = 9.4204$ (3) Å

 $c = 10.4347$ (4) Å

 $\alpha = 72.733$ (2)°

 $\beta = 74.152$ (2)°

 $\gamma = 70.250$ (2)°

 $V = 654.05$ (4) Å³
 $Z = 2$

 Mo $K\alpha$ radiation

 $\mu = 0.28$ mm⁻¹
 $T = 150$ K

 $0.13 \times 0.12 \times 0.09$ mm

Data collection

Nonius KappaCCD diffractometer

Absorption correction: none

5719 measured reflections

3073 independent reflections

 2601 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.016$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.036$
 $wR(F^2) = 0.035$
 $S = 1.10$

2491 reflections

145 parameters

H-atom parameters constrained

 $\Delta\rho_{\text{max}} = 0.25$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.20$ e Å⁻³
Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{N2}-\text{H3}\cdots\text{Cl1}$	0.90	2.18	3.069 (1)	169
$\text{N2}-\text{H4}\cdots\text{O1}^{\text{i}}$	0.91	1.86	2.776 (2)	175
$\text{O1}-\text{H1}\cdots\text{Cl1}$	0.82	2.32	3.120 (1)	165
$\text{O1}-\text{H2}\cdots\text{Cl1}^{\text{ii}}$	0.83	2.31	3.136 (1)	171
$\text{C10}-\text{H15}\cdots\text{Cl1}^{\text{iii}}$	0.99	2.87	3.846 (1)	168
$\text{C12}-\text{H20}\cdots\text{Cl1}^{\text{iv}}$	0.97	2.84	3.779 (3)	161
$\text{C12}-\text{H19}\cdots\text{O1}^{\text{v}}$	0.99	2.73	3.448 (2)	130

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

Data collection: *COLLECT* (Nonius, 2001); cell refinement: *DENZO/SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO/SCALEPACK*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *CRYSTALS* (Betteridge *et al.*, 2003); molecular graphics: *DIAMOND* (Brandenburg, 1998); software used to prepare material for publication: *CRYSTALS*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: CF2207).

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supporting information

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4-(2,3-Dimethylphenyl)piperazin-1-ium chloride monohydrate

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S1. Comment

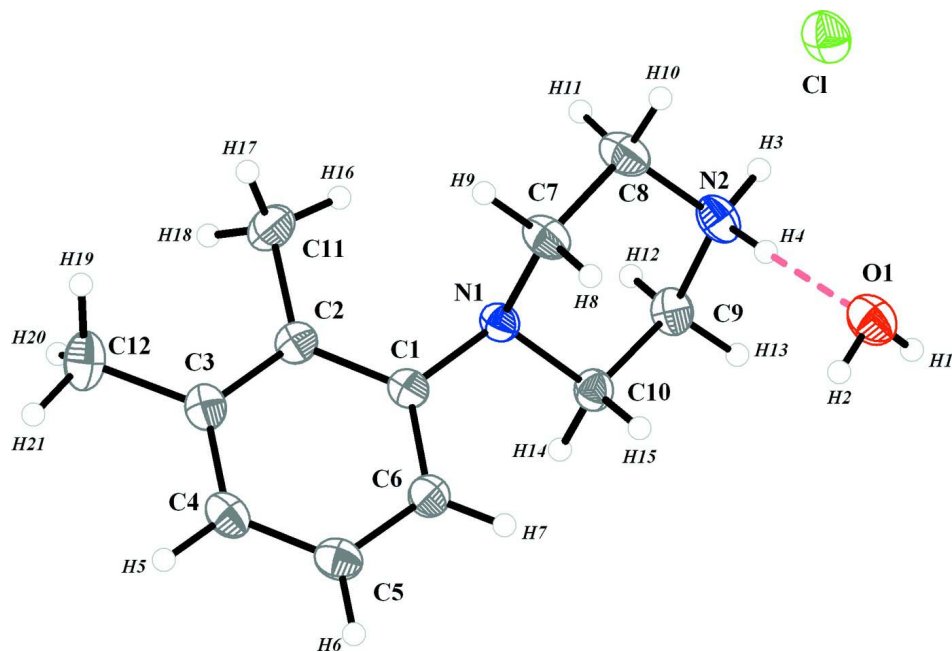
The coordination chemistry of anions is a fast-growing area of supramolecular chemistry (Schmidtchen & Berge, 1997), on account of the importance of anion binding, recognition and transport in many biochemical processes (Pajewski *et al.*, 2004). Thus, the Cl⁻ anion has been successfully used to assemble double-helical motifs of various molecules (Sessler *et al.*, 2003). Here a new member of this family, the title compound, is presented, which was obtained during our studies of the preparation of new organic hydrochloride compounds. As shown in Fig. 1, the asymmetric unit of the crystal structure of the title compound contains a 4-(2,3-dimethylphenyl)piperazin-1-ium cation, a chloride anion and a water molecule, associated in a hydrogen-bonded network. Two water molecules and two Cl⁻ anions are interconnected through O—H...Cl hydrogen bonds, forming an 8-membered ring with graph-set $R_2^4(8)$ Bernstein *et al.*, 1995). These entities are connected to two antiparallel organic cations *via* N—H...Cl, N—H...O and C—H...Cl hydrogen-bonding interactions to construct a convoluted hydrogen-bonded chain which runs in the *c*-axis direction (Fig. 2). When projected along the *b* axis, the chains have a marked zigzag structure and somewhat resemble a helix (Fig. 3). In addition to the hydrogen-bonding associations to Cl1 and O1, the organic cations have a second role by linking these chains to each other to form layers parallel to the *bc* plane through C—H...O hydrogen bonds. Fig. 3 shows that these planes are interconnected by NH₂⁺ groups to form an open framework architecture through hydrogen-bond interactions. An examination of the organic group geometrical features shows that the carbon atoms in the benzene ring of the title compound have a good coplanarity and they form a conjugated ring with an average deviation of 0.013 Å. The mean value of the C—C bond lengths [1.3967 (17) Å], which is between a single bond and a double bond, agrees with that in phenylpiperazinium tetrachloridozincate(II) [1.384 (4) Å] (Ben Gharbia *et al.*, 2005). The piperazine-1,4-dium ring of the title compound adopts a typical chair conformation and its geometric parameters [$d_{av}(C—N) = 1.4818$ (16) and $d_{av}(C—C) = 1.5437$ (17) Å] are in full agreement with those found in 4-(2,3-dimethylphenyl)piperazin-1-ium tetrachloridozincate(II) (Ben Gharbia *et al.*, 2007).

S2. Experimental

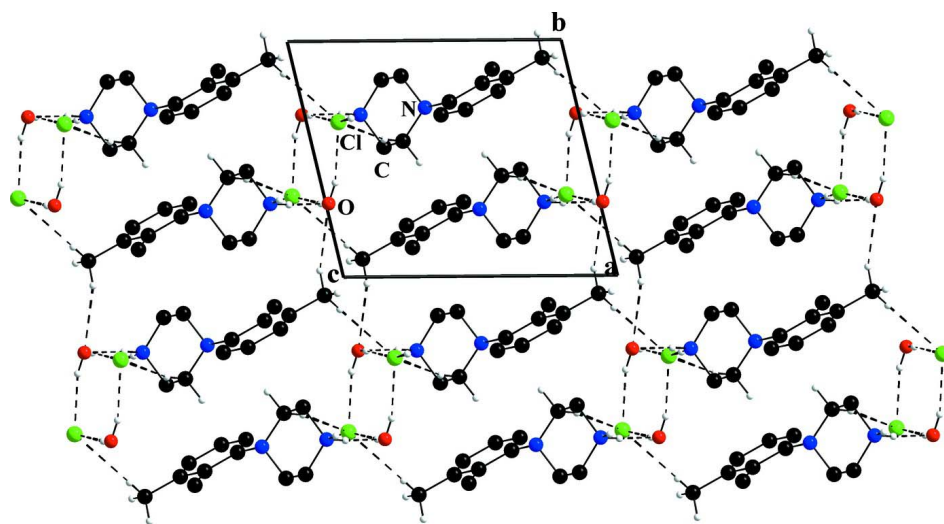
An aqueous 1M HCl solution and 1-(2,3-dimethylphenyl)piperazine in a 1:1 molar ratio were mixed and dissolved in sufficient ethanol. Crystals of (I) grew as the ethanol evaporated at 293 K over the course of a few days.

S3. Refinement

The H atoms were all located in a difference map, but those attached to carbon atoms were repositioned geometrically. The H atoms were initially refined with soft restraints on the bond lengths and angles to regularize their geometry (C—H in the range 0.93–0.98, N—H in the range 0.86–0.89 and O—H = 0.82 Å) and $U_{iso}(H)$ (in the range 1.2–1.5 times U_{eq} of the parent atom), after which the positions were refined with riding constraints. Low-angle reflections possibly affected by the beam-stop and some other outliers were omitted from the refinement.

**Figure 1**

The asymmetric unit of (I), showing 40% probability displacement ellipsoids.

**Figure 2**

The packing of (I), viewed down the *a* axis, showing the O—H \cdots Cl, N—H \cdots Cl, N—H \cdots O, C—H \cdots O and C—H \cdots Cl interactions (dashed lines) between the 4-(2,3-dimethylphenyl)piperazin-1-ium cation, water molecule and chloride anion.

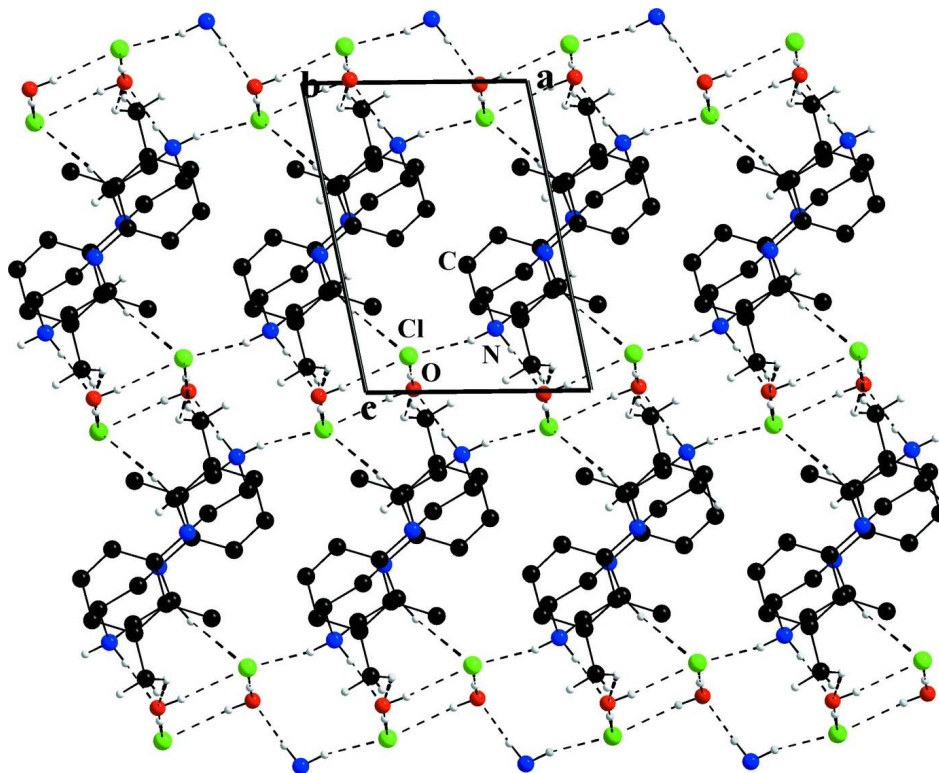


Figure 3

The packing of (I), viewed down the *b* axis, showing the zigzag character of the structure. Hydrogen bonds are indicated by dashed lines.

4-(2,3-Dimethylphenyl)piperazin-1-ium chloride monohydrate

Crystal data

$C_{12}H_{19}N_2^+ \cdot Cl^- \cdot H_2O$

$M_r = 244.76$

Triclinic, $P\bar{1}$

Hall symbol: $-P\ 1$

$a = 7.5439\ (3)\ \text{\AA}$

$b = 9.4204\ (3)\ \text{\AA}$

$c = 10.4347\ (4)\ \text{\AA}$

$\alpha = 72.733\ (2)^\circ$

$\beta = 74.152\ (2)^\circ$

$\gamma = 70.250\ (2)^\circ$

$V = 654.05\ (4)\ \text{\AA}^3$

$Z = 2$

$F(000) = 264$

$D_x = 1.243\ \text{Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71069\ \text{\AA}$

Cell parameters from 2750 reflections

$\theta = 0.4\text{--}27.9^\circ$

$\mu = 0.28\ \text{mm}^{-1}$

$T = 150\ \text{K}$

Block, colorless

$0.13 \times 0.12 \times 0.09\ \text{mm}$

Data collection

Nonius KappaCCD

diffractometer

Graphite monochromator

φ and ω scans

5719 measured reflections

3073 independent reflections

2601 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.016$

$\theta_{\text{max}} = 27.9^\circ$, $\theta_{\text{min}} = 2.1^\circ$

$h = -9 \rightarrow 9$

$k = -12 \rightarrow 12$

$l = -13 \rightarrow 13$

*Refinement*Refinement on F

Least-squares matrix: full

 $R[F^2 > 2\sigma(F^2)] = 0.036$ $wR(F^2) = 0.035$ $S = 1.10$

2491 reflections

145 parameters

0 restraints

Primary atom site location: structure-invariant
direct methodsHydrogen site location: inferred from
neighbouring sites

H-atom parameters constrained

 $w = [1 - (F_o - F_c)^2 / 36\sigma^2(F)]^2 / [0.443T_0(x) +$
 $0.129T_1(x) + 0.131T_2(x)]$ where T_i are Chebychev polynomials and $x =$ F_o/F_{\max} (Prince, 1982; Watkin, 1994) $(\Delta/\sigma)_{\max} = 0.000359$ $\Delta\rho_{\max} = 0.25 \text{ e } \text{\AA}^{-3}$ $\Delta\rho_{\min} = -0.20 \text{ e } \text{\AA}^{-3}$ *Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)*

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	-0.09326 (17)	0.26100 (14)	0.53871 (13)	0.0211
C2	-0.08069 (18)	0.18226 (14)	0.67481 (13)	0.0224
C3	-0.24822 (19)	0.15986 (14)	0.76843 (13)	0.0243
C4	-0.42381 (18)	0.21709 (15)	0.72522 (14)	0.0270
C5	-0.43454 (18)	0.29399 (16)	0.59077 (14)	0.0285
C6	-0.26999 (18)	0.31526 (15)	0.49687 (13)	0.0255
C7	0.18840 (18)	0.14963 (15)	0.38467 (14)	0.0276
C8	0.38588 (19)	0.16564 (16)	0.30991 (15)	0.0313
C9	0.24578 (19)	0.45044 (15)	0.26085 (13)	0.0260
C10	0.05184 (17)	0.42554 (14)	0.33543 (13)	0.0230
C11	0.1080 (2)	0.12337 (17)	0.72288 (15)	0.0320
C12	-0.2398 (2)	0.07656 (18)	0.91485 (14)	0.0353
Cl1	0.77820 (5)	0.34324 (4)	0.11653 (4)	0.0340
O1	0.78625 (14)	0.68790 (12)	0.00994 (10)	0.0353
N1	0.07922 (14)	0.28419 (12)	0.44468 (11)	0.0216
N2	0.36750 (15)	0.31276 (13)	0.20308 (12)	0.0278
H1	0.7848	0.5995	0.0526	0.0528*
H2	0.9007	0.6873	-0.0182	0.0528*
H3	0.4845	0.3270	0.1661	0.0430*
H4	0.3144	0.3085	0.1358	0.0437*
H5	-0.5385	0.2058	0.7916	0.0322*
H6	-0.5565	0.3352	0.5610	0.0341*
H7	-0.2770	0.3659	0.4045	0.0295*
H8	0.1198	0.1410	0.3200	0.0321*
H9	0.2040	0.0561	0.4575	0.0315*
H10	0.4588	0.0790	0.2644	0.0369*
H11	0.4582	0.1695	0.3749	0.0356*
H12	0.3114	0.4642	0.3220	0.0314*
H13	0.2299	0.5429	0.1850	0.0309*
H14	-0.0266	0.5162	0.3773	0.0269*
H15	-0.0141	0.4180	0.2684	0.0273*
H16	0.2087	0.1594	0.6514	0.0467*
H17	0.1484	0.0098	0.7464	0.0473*
H18	0.0940	0.1606	0.8047	0.0484*

H19	-0.1476	-0.0282	0.9197	0.0537*
H20	-0.2011	0.1364	0.9587	0.0526*
H21	-0.3671	0.0679	0.9639	0.0532*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0204 (5)	0.0193 (5)	0.0239 (6)	-0.0065 (4)	-0.0025 (4)	-0.0057 (5)
C2	0.0250 (6)	0.0184 (5)	0.0251 (6)	-0.0079 (5)	-0.0054 (5)	-0.0040 (5)
C3	0.0289 (6)	0.0211 (6)	0.0243 (6)	-0.0104 (5)	-0.0022 (5)	-0.0059 (5)
C4	0.0243 (6)	0.0269 (6)	0.0298 (7)	-0.0099 (5)	0.0020 (5)	-0.0098 (5)
C5	0.0213 (6)	0.0308 (7)	0.0331 (7)	-0.0073 (5)	-0.0039 (5)	-0.0081 (6)
C6	0.0231 (6)	0.0273 (6)	0.0250 (6)	-0.0079 (5)	-0.0040 (5)	-0.0040 (5)
C7	0.0241 (6)	0.0215 (6)	0.0347 (7)	-0.0077 (5)	0.0025 (5)	-0.0088 (5)
C8	0.0229 (6)	0.0274 (7)	0.0392 (8)	-0.0073 (5)	0.0025 (5)	-0.0088 (6)
C9	0.0289 (6)	0.0260 (6)	0.0255 (6)	-0.0128 (5)	-0.0024 (5)	-0.0061 (5)
C10	0.0236 (6)	0.0224 (6)	0.0220 (6)	-0.0081 (5)	-0.0026 (5)	-0.0034 (5)
C11	0.0286 (7)	0.0337 (7)	0.0317 (7)	-0.0115 (6)	-0.0113 (5)	0.0038 (6)
C12	0.0452 (8)	0.0378 (8)	0.0246 (7)	-0.0210 (7)	-0.0034 (6)	-0.0016 (6)
C11	0.02788 (17)	0.0430 (2)	0.03519 (18)	-0.01831 (14)	-0.00224 (13)	-0.00861 (14)
O1	0.0303 (5)	0.0377 (6)	0.0367 (5)	-0.0128 (4)	0.0007 (4)	-0.0094 (4)
N1	0.0205 (5)	0.0191 (5)	0.0234 (5)	-0.0059 (4)	-0.0013 (4)	-0.0044 (4)
N2	0.0229 (5)	0.0332 (6)	0.0291 (6)	-0.0136 (4)	0.0028 (4)	-0.0101 (5)

Geometric parameters (Å, °)

C9—C10	1.5176 (17)	C6—H7	0.947
C9—N2	1.4986 (17)	C5—C4	1.3851 (19)
C9—H12	0.966	C5—H6	0.968
C9—H13	0.985	C4—C3	1.3957 (19)
C10—N1	1.4686 (16)	C4—H5	0.965
C10—H14	1.005	C3—C2	1.4070 (17)
C10—H15	0.993	C3—C12	1.5038 (19)
C7—C8	1.5159 (17)	C2—C11	1.5090 (17)
C7—N1	1.4701 (16)	C12—H21	0.975
C7—H9	0.974	C12—H20	0.974
C7—H8	0.991	C12—H19	0.993
C8—N2	1.4900 (18)	C11—H18	0.983
C8—H11	0.995	C11—H16	0.981
C8—H10	0.989	C11—H17	0.981
C1—C6	1.3979 (17)	O1—H1	0.822
C1—C2	1.4060 (17)	O1—H2	0.831
C1—N1	1.4391 (15)	N2—H3	0.900
C6—C5	1.3886 (18)	N2—H4	0.914
C10—C9—N2	109.56 (10)	C4—C5—H6	120.8
C10—C9—H12	111.0	C5—C4—C3	120.72 (12)
N2—C9—H12	108.8	C5—C4—H5	120.5

C10—C9—H13	110.3	C3—C4—H5	118.7
N2—C9—H13	108.5	C4—C3—C2	119.63 (12)
H12—C9—H13	108.6	C4—C3—C12	119.84 (12)
C9—C10—N1	109.41 (10)	C2—C3—C12	120.53 (12)
C9—C10—H14	109.0	C3—C2—C1	119.20 (11)
N1—C10—H14	108.9	C3—C2—C11	119.40 (12)
C9—C10—H15	108.6	C1—C2—C11	121.39 (11)
N1—C10—H15	111.3	C3—C12—H21	109.5
H14—C10—H15	109.6	C3—C12—H20	109.5
C8—C7—N1	110.04 (10)	H21—C12—H20	107.6
C8—C7—H9	108.4	C3—C12—H19	110.4
N1—C7—H9	109.2	H21—C12—H19	109.8
C8—C7—H8	109.4	H20—C12—H19	109.9
N1—C7—H8	110.2	C2—C11—H18	109.7
H9—C7—H8	109.5	C2—C11—H16	110.8
C7—C8—N2	109.88 (11)	H18—C11—H16	109.0
C7—C8—H11	110.1	C2—C11—H17	110.4
N2—C8—H11	107.8	H18—C11—H17	108.5
C7—C8—H10	111.2	H16—C11—H17	108.4
N2—C8—H10	108.0	H1—O1—H2	107.1
H11—C8—H10	109.9	C7—N1—C10	109.62 (10)
C6—C1—C2	120.31 (11)	C7—N1—C1	112.16 (9)
C6—C1—N1	121.24 (11)	C10—N1—C1	115.19 (10)
C2—C1—N1	118.45 (11)	C9—N2—C8	112.04 (10)
C1—C6—C5	119.86 (12)	C9—N2—H3	107.5
C1—C6—H7	119.9	C8—N2—H3	109.3
C5—C6—H7	120.2	C9—N2—H4	108.6
C6—C5—C4	120.27 (12)	C8—N2—H4	110.2
C6—C5—H6	118.9	H3—N2—H4	109.1

Hydrogen-bond geometry (Å, °)

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N2—H3...C11	0.90	2.18	3.069 (1)	169
N2—H4...O1 ⁱ	0.91	1.86	2.776 (2)	175
O1—H1...C11	0.82	2.32	3.120 (1)	165
O1—H2...C11 ⁱⁱ	0.83	2.31	3.136 (1)	171
C10—H15...C11 ⁱⁱⁱ	0.99	2.87	3.846 (1)	168
C12—H20...C11 ^{iv}	0.97	2.84	3.779 (3)	161
C12—H19...O1 ^v	0.99	2.73	3.448 (2)	130

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