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# 4-(4-Chlorophenyl)-4-hydroxypiperidinium maleate maleic acid solvate

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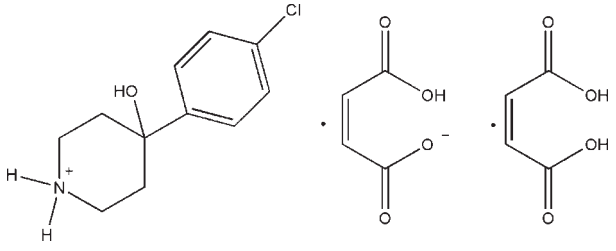
Key indicators: single-crystal X-ray study; $T$ = 100 K; mean $\sigma$(C–C) = 0.002 Å; $R$ factor = 0.034; $wR$ factor = 0.092; data-to-parameter ratio = 20.0.

In the cation of the title compound, $C_{11}H_{15}ClNO^+\cdot C_4H_3O_4^-\cdot C_4H_4O_4$, the dihedral angle between the mean planes of the chlorine-substituted aromatic ring and the 4-hydroxypiperidinium ring (C–C–C–C–C–N) is 61.9 (8)°. Intramolecular O—H···O and intermolecular O—H···O and N—H···O hydrogen bonding, as well as weak $\pi$-stacking interactions [centroid–centroid distance = 3.646 (5) Å] help to establish the packing.

## Related literature

For the synthesis and biological activity of uncondensed cyclic derivatives of piperidine, see: Vartanyan (1984). For related structures, see: James & Williams (1974); Bertolasi *et al.* (1980); Dawson *et al.* (1986); Vyas *et al.* (1999); Kiang *et al.* (2003); Trask *et al.* (2005); Mohamed *et al.* (2009); Dutkiewicz *et al.* (2010); Fun *et al.* (2010); Jasinski *et al.* (2010). For bond-length data, see: Allen *et al.* (1987). For puckering parameters, see: Cremer & Pople (1975).




## Experimental

### Crystal data

$C_{11}H_{15}ClNO^+\cdot C_4H_3O_4^-\cdot C_4H_4O_4$
$M_r$ = 443.83
Monoclinic, $C2/c$
$a$ = 19.282 (7) Å
$b$ = 7.867 (3) Å
$c$ = 25.115 (9) Å
$\beta$ = 91.545 (5)°
$V$ = 3808 (2) Å$^3$
$Z$ = 8
Mo $K\alpha$ radiation
$\mu$ = 0.26 mm$^{-1}$
$T$ = 100 K
0.52 × 0.41 × 0.39 mm

### Data collection

Bruker APEXII CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2008)
$T_{min}$ = 0.878, $T_{max}$ = 0.907
18187 measured reflections
5841 independent reflections
5194 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.021

### Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.034
$wR(F^2)$ = 0.092
$S$ = 1.03
5841 reflections
292 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.48 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.23 e Å$^{-3}$

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| O1$C$—H1$C$···O2$B^{i}$ | 0.82 | 1.97 | 2.7852 (13) | 171 |
| O1$A$—H2$A$···O1$B^{ii}$ | 0.90 (2) | 1.68 (2) | 2.5546 (13) | 162 (2) |
| N1$C$—H13$C$···O3$B^{iii}$ | 0.890 (17) | 1.954 (18) | 2.8328 (14) | 168.6 (16) |
| N1$C$—H14$C$···O2$A^{iv}$ | 0.887 (17) | 2.087 (17) | 2.9144 (15) | 154.9 (15) |
| O4$A$—H1$A$···O3$A$ | 0.91 (2) | 1.65 (2) | 2.5531 (13) | 173.7 (19) |
| O3$B$—H1$B$···O4$B$ | 1.18 (2) | 1.23 (2) | 2.4108 (12) | 177 (2) |

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

Data collection: *APEX2* (Bruker, 2008); cell refinement: *SAINT* (Bruker, 2008); 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: WM2372).

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# supplementary materials

*Acta Cryst.* (2010). E**66**, o2012-o2013 [ **doi:10.1107/S1600536810026917** ]

# 4-(4-Chlorophenyl)-4-hydroxypiperidinium maleate maleic acid solvate

**J. P. Jasinski, A. E. Pek, B. P. Siddaraju, H. S. Yathirajan and B. Narayana**

## Comment

4-(4-Chlorophenyl)-4-hydroxypiperidine is used as an intermediate for the synthesis of pharmaceuticals such as haloperidol (a neuroleptic drug used to treat patients with psychotic illnesses, extreme agitation, or Tourette's syndrome) and loperamide which is a synthetic piperidine derivative and a drug effective against diarrhea resulting from gastroenteritis or inflammatory bowel disease. A review on the synthesis and biological activity of uncondensed cyclic derivatives of piperidine is reported (Vartanyan, 1984). A study of the structural chemistry of maleic acid and related substances arises from the fact that these systems possess short but highly strained hydrogen bonds (James & Williams, 1974). The crystal structures of maleic acid (James & Williams, 1974), carbinoxamine maleate (Bertolasi *et al.*, 1980), [2-(2,2-dicyclohexylethyl) piperidine] maleate (Dawson *et al.*, 1986), domeperidone maleate (Vyas *et al.*, 1999), enalapril maleate (Kiang *et al.*, 2003), 1:1 co-crystal of caffeine with maleic acid (Trask *et al.*, 2005), 4-dimethylaminopyridinium maleate (Mohamed *et al.*, 2009), 4-(4-chlorophenyl)piperidin-4-ol (Dutkiewicz *et al.*, 2010), bis[4-(4-chlorophenyl)-4-hydroxypiperidinium] dipicrate dimethyl sulfoxide solvate (Fun *et al.*, 2010) and trimipraminium maleate (Jasinski *et al.*, 2010) have been reported. In view of the importance of salts of piperidines, this paper reports the crystal structure of the title compound, $C_{11}H_{15}Cl\,N\,O^{+}$, $C_4H_3O_4^{-}$, $C_4H_4O_4$.

The asymmetric unit of the title compound (Fig.1) contains one 4-(4-chlorophenyl)-4-hydroxypiperidinium cation, one maleate anion, and one maleic acid molecule. The protonated 4-hydroxypiperidinium cation is in a chair conformation (puckering parameters Q, θ, and φ = 0.576 (2) Å, 179.0 (8)° and 159.955 (0)°, respectively; (Cremer & Pople, 1975). For an ideal chair θ has a value of 0 or 180°). Bond distances and angles are in normal ranges (Allen *et al.*, 1987). The dihedral angle between the mean planes of the piperidinium ring in the cation (C7C/C8C/C9C/C10C/C11C/N1C) and the benzene ring (C1—C6) is 61.9 (8)°. Strong intramolecular O—H···O and intermolecular O—H···O, N—H···O hydrogen bonding interactions (Table 1, Fig. 2) dominate the crystal packing which leads to the formation of chains along [010]. In addition, weak π-stacking intermolecular interactions occur between symmetry related benzene rings (Table 2) which also influence the crystal packing.

## Experimental

4-(4-chlorophenyl)-piperidin-4-ol (2.2 g, 0.01 mol) and maleic acid (1.16 g, 0.01 mol) were dissolved in 20 ml of methanol. The mixture was stirred for 30 minutes at 333 K. Then the solution was kept aside for 3 days at room temperature. Yellow crystals were obtained (m.p: 381–383 K) by slow evaporation of methanol solution.

## Refinement

The hydroxyl H atoms, H1A, H2A, H1B, H1C and N H atoms, H13C, H14C, were located by a Fourier map. These H atoms and the rest of the H atoms were then positioned geometrically and allowed to ride on their parent atoms with *X*—H lengths of 0.91Å (O4A), 0.90Å (O1A), 1.18Å (O3B), 0.82Å (O1C), 0.89–0.89Å (N1C), 0.93Å (CH) or 0.97Å ($CH_2$). Isotropic

displacement parameters for these atoms were set to 1.4–3.5 times (OH), 1.8 times (NH), 1.20 (CH) or 1.2 ($CH_2$) times $U_{eq}$ of the parent atom.

**Figures**

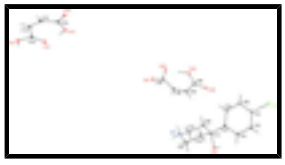

Fig. 1. Molecular structures of the $C_{11}H_{15}ClNO^+$, $C_4H_3O_4^-$ and $C_4H_4O_4$ entities, showing the atom labeling scheme and 30% probability displacement ellipsoids.

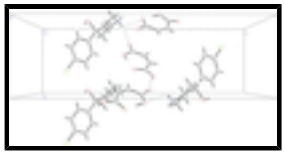

Fig. 2. Packing diagram of the title compound $C_{11}H_{15}ClNO^+$, $C_4H_3O_4^-$, $C_4H_4O_4$, viewed down [100].

**4-(4-Chlorophenyl)-4-hydroxypiperidinium maleate maleic acid solvate**

*Crystal data*

| | |
|---|---|
| $C_{11}H_{15}ClNO^+·C_4H_3O_4^-·C_4H_4O_4$ | $F(000) = 1856$ |
| $M_r = 443.83$ | $D_x = 1.548$ Mg m$^{-3}$ |
| Monoclinic, $C2/c$ | Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å |
| Hall symbol: -C 2yc | Cell parameters from 8484 reflections |
| $a = 19.282$ (7) Å | $\theta = 2.6–31.3°$ |
| $b = 7.867$ (3) Å | $\mu = 0.26$ mm$^{-1}$ |
| $c = 25.115$ (9) Å | $T = 100$ K |
| $\beta = 91.545$ (5)° | Block, yellow |
| $V = 3808$ (2) Å$^3$ | 0.52 × 0.41 × 0.39 mm |
| $Z = 8$ | |

*Data collection*

| | |
|---|---|
| Bruker APEXII CCD diffractometer | 5841 independent reflections |
| Radiation source: fine-focus sealed tube | 5194 reflections with $I > 2\sigma(I)$ |
| graphite | $R_{int} = 0.021$ |
| ω scans | $\theta_{max} = 31.3°$, $\theta_{min} = 1.6°$ |
| Absorption correction: multi-scan (*SADABS*; Bruker, 2008) | $h = -27\rightarrow27$ |
| $T_{min} = 0.878$, $T_{max} = 0.907$ | $k = -11\rightarrow11$ |
| 18187 measured reflections | $l = -35\rightarrow35$ |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | Primary atom site location: structure-invariant direct methods |
| Least-squares matrix: full | Secondary atom site location: difference Fourier map |

| | |
|---|---|
| $R[F^2 > 2\sigma(F^2)] = 0.034$ | Hydrogen site location: inferred from neighbouring sites |
| $wR(F^2) = 0.092$ | H atoms treated by a mixture of independent and constrained refinement |
| $S = 1.03$ | $w = 1/[\sigma^2(F_o^2) + (0.0463P)^2 + 3.2429P]$ where $P = (F_o^2 + 2F_c^2)/3$ |
| 5841 reflections | $(\Delta/\sigma)_{max} = 0.001$ |
| 292 parameters | $\Delta\rho_{max} = 0.48$ e Å$^{-3}$ |
| 0 restraints | $\Delta\rho_{min} = -0.23$ 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 (Å$^2$)*

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| Cl1 | 0.480203 (14) | 0.66435 (4) | 0.161617 (11) | 0.02088 (7) |
| O4B | 0.16691 (4) | 0.58804 (10) | 0.50337 (3) | 0.01619 (15) |
| O3B | 0.22900 (4) | 0.66101 (10) | 0.42453 (3) | 0.01604 (15) |
| C5B | 0.20779 (5) | 0.56565 (13) | 0.38519 (4) | 0.01359 (18) |
| C4B | 0.14848 (6) | 0.44620 (14) | 0.39300 (4) | 0.01543 (19) |
| H4B | 0.1353 | 0.3844 | 0.3628 | 0.019* |
| C2B | 0.11909 (5) | 0.47937 (13) | 0.49149 (4) | 0.01414 (19) |
| C3B | 0.11113 (6) | 0.41304 (14) | 0.43602 (4) | 0.01520 (19) |
| H3B | 0.0747 | 0.3371 | 0.4304 | 0.018* |
| O3A | 0.46151 (4) | 0.35880 (11) | 0.96021 (3) | 0.01793 (16) |
| C2A | 0.44308 (6) | 0.35385 (13) | 1.00654 (4) | 0.01452 (19) |
| C3A | 0.38419 (6) | 0.45056 (14) | 1.02827 (4) | 0.0163 (2) |
| H3A | 0.3766 | 0.4349 | 1.0644 | 0.020* |
| C5A | 0.33654 (6) | 0.61984 (14) | 0.94690 (4) | 0.01610 (19) |
| C4A | 0.34039 (6) | 0.55740 (14) | 1.00297 (4) | 0.0162 (2) |
| H4A | 0.3060 | 0.6007 | 1.0244 | 0.019* |
| O1A | 0.47414 (4) | 0.26101 (10) | 1.04317 (3) | 0.01712 (16) |
| O2A | 0.29197 (4) | 0.72438 (11) | 0.93499 (3) | 0.02023 (17) |
| O1B | 0.07936 (4) | 0.42630 (10) | 0.52580 (3) | 0.01788 (16) |
| O2B | 0.23403 (4) | 0.57247 (10) | 0.34108 (3) | 0.01693 (16) |
| C4C | 0.37887 (5) | 0.24201 (13) | 0.25343 (4) | 0.01180 (18) |
| C1C | 0.44091 (5) | 0.50191 (14) | 0.19706 (4) | 0.01430 (19) |
| C6C | 0.39980 (5) | 0.54258 (13) | 0.23944 (4) | 0.01428 (19) |

| | | | | |
|---|---|---|---|---|
| H6C | 0.3928 | 0.6554 | 0.2490 | 0.017* |
| C5C | 0.36902 (5) | 0.41155 (13) | 0.26767 (4) | 0.01336 (18) |
| H5C | 0.3415 | 0.4374 | 0.2964 | 0.016* |
| C3C | 0.42116 (5) | 0.20613 (14) | 0.21058 (4) | 0.01490 (19) |
| H3C | 0.4287 | 0.0936 | 0.2010 | 0.018* |
| C2C | 0.45221 (6) | 0.33510 (14) | 0.18203 (4) | 0.0161 (2) |
| H2C | 0.4800 | 0.3100 | 0.1534 | 0.019* |
| O1C | 0.33643 (4) | −0.04881 (10) | 0.24944 (3) | 0.01551 (15) |
| H1C | 0.3122 | −0.0211 | 0.2235 | 0.023* |
| C10C | 0.39685 (5) | 0.03445 (13) | 0.32796 (4) | 0.01363 (18) |
| H10A | 0.4395 | −0.0037 | 0.3123 | 0.016* |
| H10B | 0.4080 | 0.1291 | 0.3514 | 0.016* |
| C8C | 0.27733 (5) | 0.14407 (13) | 0.30800 (4) | 0.01358 (18) |
| H8C1 | 0.2841 | 0.2427 | 0.3307 | 0.016* |
| H8C2 | 0.2444 | 0.1744 | 0.2797 | 0.016* |
| C7C | 0.34665 (5) | 0.09495 (13) | 0.28369 (4) | 0.01154 (17) |
| C9C | 0.36671 (5) | −0.10930 (14) | 0.36035 (4) | 0.01464 (19) |
| H9C1 | 0.3594 | −0.2083 | 0.3379 | 0.018* |
| H9C2 | 0.3989 | −0.1401 | 0.3891 | 0.018* |
| C11C | 0.24805 (5) | −0.00126 (14) | 0.34043 (4) | 0.01492 (19) |
| H11A | 0.2054 | 0.0348 | 0.3566 | 0.018* |
| H11B | 0.2374 | −0.0968 | 0.3172 | 0.018* |
| N1C | 0.29935 (5) | −0.05450 (12) | 0.38279 (3) | 0.01394 (17) |
| O4A | 0.38012 (5) | 0.56565 (12) | 0.91126 (3) | 0.02079 (17) |
| H13C | 0.2810 (9) | −0.142 (2) | 0.3999 (7) | 0.026 (4)* |
| H14C | 0.3072 (8) | 0.031 (2) | 0.4050 (7) | 0.024 (4)* |
| H1A | 0.4103 (10) | 0.490 (3) | 0.9264 (8) | 0.042 (5)* |
| H2A | 0.5113 (11) | 0.206 (3) | 1.0307 (8) | 0.049 (6)* |
| H1B | 0.1992 (12) | 0.629 (3) | 0.4638 (9) | 0.059 (6)* |

*Atomic displacement parameters (Å$^2$)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Cl1 | 0.01862 (13) | 0.02183 (14) | 0.02233 (13) | −0.00193 (9) | 0.00295 (9) | 0.01083 (10) |
| O4B | 0.0190 (4) | 0.0170 (4) | 0.0125 (3) | −0.0050 (3) | −0.0001 (3) | −0.0003 (3) |
| O3B | 0.0197 (4) | 0.0149 (4) | 0.0136 (3) | −0.0050 (3) | 0.0016 (3) | −0.0013 (3) |
| C5B | 0.0153 (4) | 0.0120 (4) | 0.0134 (4) | 0.0008 (3) | −0.0006 (3) | 0.0011 (3) |
| C4B | 0.0185 (5) | 0.0139 (5) | 0.0138 (4) | −0.0022 (4) | −0.0015 (4) | −0.0018 (3) |
| C2B | 0.0158 (5) | 0.0126 (4) | 0.0139 (4) | −0.0002 (4) | −0.0009 (3) | 0.0011 (3) |
| C3B | 0.0172 (5) | 0.0140 (5) | 0.0143 (4) | −0.0022 (4) | −0.0017 (4) | −0.0009 (3) |
| O3A | 0.0202 (4) | 0.0188 (4) | 0.0150 (3) | 0.0024 (3) | 0.0031 (3) | 0.0004 (3) |
| C2A | 0.0154 (5) | 0.0122 (4) | 0.0160 (4) | −0.0015 (3) | 0.0007 (3) | −0.0003 (3) |
| C3A | 0.0191 (5) | 0.0153 (5) | 0.0146 (4) | 0.0008 (4) | 0.0027 (4) | 0.0000 (4) |
| C5A | 0.0168 (5) | 0.0136 (5) | 0.0178 (5) | −0.0020 (4) | −0.0011 (4) | 0.0008 (4) |
| C4A | 0.0171 (5) | 0.0145 (5) | 0.0170 (5) | 0.0005 (4) | 0.0022 (4) | −0.0005 (4) |
| O1A | 0.0181 (4) | 0.0173 (4) | 0.0159 (3) | 0.0041 (3) | 0.0010 (3) | 0.0013 (3) |
| O2A | 0.0195 (4) | 0.0164 (4) | 0.0246 (4) | 0.0012 (3) | −0.0029 (3) | 0.0038 (3) |
| O1B | 0.0198 (4) | 0.0188 (4) | 0.0151 (3) | −0.0042 (3) | 0.0025 (3) | 0.0011 (3) |

| | | | | | | |
|---|---|---|---|---|---|---|
| O2B | 0.0191 (4) | 0.0187 (4) | 0.0131 (3) | −0.0003 (3) | 0.0019 (3) | 0.0003 (3) |
| C4C | 0.0123 (4) | 0.0121 (4) | 0.0110 (4) | −0.0001 (3) | −0.0002 (3) | 0.0005 (3) |
| C1C | 0.0122 (4) | 0.0171 (5) | 0.0136 (4) | −0.0018 (4) | −0.0003 (3) | 0.0057 (4) |
| C6C | 0.0151 (4) | 0.0124 (4) | 0.0154 (4) | −0.0006 (4) | 0.0004 (3) | 0.0013 (3) |
| C5C | 0.0152 (4) | 0.0129 (4) | 0.0122 (4) | −0.0001 (3) | 0.0023 (3) | −0.0003 (3) |
| C3C | 0.0155 (5) | 0.0144 (5) | 0.0149 (4) | 0.0006 (4) | 0.0018 (3) | −0.0003 (4) |
| C2C | 0.0158 (5) | 0.0197 (5) | 0.0128 (4) | 0.0010 (4) | 0.0035 (3) | 0.0013 (4) |
| O1C | 0.0234 (4) | 0.0113 (3) | 0.0117 (3) | −0.0010 (3) | −0.0014 (3) | −0.0015 (3) |
| C10C | 0.0133 (4) | 0.0147 (5) | 0.0129 (4) | 0.0004 (3) | 0.0004 (3) | 0.0017 (3) |
| C8C | 0.0133 (4) | 0.0128 (4) | 0.0147 (4) | 0.0006 (3) | 0.0014 (3) | 0.0030 (3) |
| C7C | 0.0139 (4) | 0.0100 (4) | 0.0107 (4) | −0.0004 (3) | 0.0006 (3) | −0.0003 (3) |
| C9C | 0.0161 (5) | 0.0143 (5) | 0.0135 (4) | 0.0015 (4) | 0.0005 (3) | 0.0019 (3) |
| C11C | 0.0133 (4) | 0.0160 (5) | 0.0154 (4) | −0.0015 (4) | 0.0002 (3) | 0.0033 (4) |
| N1C | 0.0172 (4) | 0.0136 (4) | 0.0110 (4) | −0.0017 (3) | 0.0011 (3) | 0.0011 (3) |
| O4A | 0.0230 (4) | 0.0236 (4) | 0.0157 (4) | 0.0043 (3) | 0.0010 (3) | 0.0026 (3) |

*Geometric parameters (Å, °)*

| | | | |
|---|---|---|---|
| Cl1—C1C | 1.7424 (11) | C1C—C2C | 1.3844 (16) |
| O4B—C2B | 1.2865 (13) | C6C—C5C | 1.3929 (14) |
| O4B—H1B | 1.23 (2) | C6C—H6C | 0.9300 |
| O3B—C5B | 1.2978 (13) | C5C—H5C | 0.9300 |
| O3B—H1B | 1.18 (2) | C3C—C2C | 1.3876 (15) |
| C5B—O2B | 1.2315 (13) | C3C—H3C | 0.9300 |
| C5B—C4B | 1.4972 (15) | C2C—H2C | 0.9300 |
| C4B—C3B | 1.3403 (15) | O1C—C7C | 1.4314 (12) |
| C4B—H4B | 0.9300 | O1C—H1C | 0.8200 |
| C2B—O1B | 1.2408 (13) | C10C—C9C | 1.5178 (15) |
| C2B—C3B | 1.4917 (15) | C10C—C7C | 1.5301 (15) |
| C3B—H3B | 0.9300 | C10C—H10A | 0.9700 |
| O3A—C2A | 1.2265 (13) | C10C—H10B | 0.9700 |
| C2A—O1A | 1.3072 (13) | C8C—C11C | 1.5212 (15) |
| C2A—C3A | 1.4830 (15) | C8C—C7C | 1.5339 (15) |
| C3A—C4A | 1.3396 (16) | C8C—H8C1 | 0.9700 |
| C3A—H3A | 0.9300 | C8C—H8C2 | 0.9700 |
| C5A—O2A | 1.2209 (14) | C9C—N1C | 1.4932 (14) |
| C5A—O4A | 1.3153 (14) | C9C—H9C1 | 0.9700 |
| C5A—C4A | 1.4912 (16) | C9C—H9C2 | 0.9700 |
| C4A—H4A | 0.9300 | C11C—N1C | 1.4930 (14) |
| O1A—H2A | 0.90 (2) | C11C—H11A | 0.9700 |
| C4C—C5C | 1.3952 (15) | C11C—H11B | 0.9700 |
| C4C—C3C | 1.3965 (14) | N1C—H13C | 0.890 (17) |
| C4C—C7C | 1.5255 (14) | N1C—H14C | 0.887 (17) |
| C1C—C6C | 1.3816 (15) | O4A—H1A | 0.91 (2) |
| C2B—O4B—H1B | 111.1 (10) | C1C—C2C—C3C | 118.61 (10) |
| C5B—O3B—H1B | 111.1 (11) | C1C—C2C—H2C | 120.7 |
| O2B—C5B—O3B | 122.07 (10) | C3C—C2C—H2C | 120.7 |
| O2B—C5B—C4B | 118.62 (9) | C7C—O1C—H1C | 109.5 |
| O3B—C5B—C4B | 119.30 (9) | C9C—C10C—C7C | 112.16 (9) |

| | | | |
|---|---|---|---|
| C3B—C4B—C5B | 131.05 (10) | C9C—C10C—H10A | 109.2 |
| C3B—C4B—H4B | 114.5 | C7C—C10C—H10A | 109.2 |
| C5B—C4B—H4B | 114.5 | C9C—C10C—H10B | 109.2 |
| O1B—C2B—O4B | 120.98 (10) | C7C—C10C—H10B | 109.2 |
| O1B—C2B—C3B | 118.74 (10) | H10A—C10C—H10B | 107.9 |
| O4B—C2B—C3B | 120.28 (9) | C11C—C8C—C7C | 111.33 (9) |
| C4B—C3B—C2B | 129.85 (10) | C11C—C8C—H8C1 | 109.4 |
| C4B—C3B—H3B | 115.1 | C7C—C8C—H8C1 | 109.4 |
| C2B—C3B—H3B | 115.1 | C11C—C8C—H8C2 | 109.4 |
| O3A—C2A—O1A | 123.13 (10) | C7C—C8C—H8C2 | 109.4 |
| O3A—C2A—C3A | 125.25 (10) | H8C1—C8C—H8C2 | 108.0 |
| O1A—C2A—C3A | 111.63 (9) | O1C—C7C—C4C | 110.55 (8) |
| C4A—C3A—C2A | 128.80 (10) | O1C—C7C—C10C | 105.37 (8) |
| C4A—C3A—H3A | 115.6 | C4C—C7C—C10C | 109.86 (8) |
| C2A—C3A—H3A | 115.6 | O1C—C7C—C8C | 109.32 (8) |
| O2A—C5A—O4A | 120.67 (10) | C4C—C7C—C8C | 112.22 (8) |
| O2A—C5A—C4A | 118.03 (10) | C10C—C7C—C8C | 109.28 (8) |
| O4A—C5A—C4A | 121.29 (10) | N1C—C9C—C10C | 109.67 (9) |
| C3A—C4A—C5A | 132.01 (10) | N1C—C9C—H9C1 | 109.7 |
| C3A—C4A—H4A | 114.0 | C10C—C9C—H9C1 | 109.7 |
| C5A—C4A—H4A | 114.0 | N1C—C9C—H9C2 | 109.7 |
| C2A—O1A—H2A | 112.2 (13) | C10C—C9C—H9C2 | 109.7 |
| C5C—C4C—C3C | 118.49 (9) | H9C1—C9C—H9C2 | 108.2 |
| C5C—C4C—C7C | 122.50 (9) | N1C—C11C—C8C | 110.12 (9) |
| C3C—C4C—C7C | 118.99 (9) | N1C—C11C—H11A | 109.6 |
| C6C—C1C—C2C | 121.83 (9) | C8C—C11C—H11A | 109.6 |
| C6C—C1C—Cl1 | 119.35 (9) | N1C—C11C—H11B | 109.6 |
| C2C—C1C—Cl1 | 118.82 (8) | C8C—C11C—H11B | 109.6 |
| C1C—C6C—C5C | 118.81 (10) | H11A—C11C—H11B | 108.1 |
| C1C—C6C—H6C | 120.6 | C11C—N1C—C9C | 112.23 (8) |
| C5C—C6C—H6C | 120.6 | C11C—N1C—H13C | 107.2 (11) |
| C6C—C5C—C4C | 120.95 (9) | C9C—N1C—H13C | 108.7 (11) |
| C6C—C5C—H5C | 119.5 | C11C—N1C—H14C | 109.4 (11) |
| C4C—C5C—H5C | 119.5 | C9C—N1C—H14C | 108.7 (10) |
| C2C—C3C—C4C | 121.30 (10) | H13C—N1C—H14C | 110.6 (15) |
| C2C—C3C—H3C | 119.3 | C5A—O4A—H1A | 110.0 (12) |
| C4C—C3C—H3C | 119.3 | | |
| O2B—C5B—C4B—C3B | 179.66 (11) | Cl1—C1C—C2C—C3C | 179.61 (8) |
| O3B—C5B—C4B—C3B | −1.76 (18) | C4C—C3C—C2C—C1C | 0.45 (16) |
| C5B—C4B—C3B—C2B | −3.5 (2) | C5C—C4C—C7C—O1C | 152.93 (9) |
| O1B—C2B—C3B—C4B | −177.70 (11) | C3C—C4C—C7C—O1C | −28.58 (13) |
| O4B—C2B—C3B—C4B | 1.50 (18) | C5C—C4C—C7C—C10C | −91.18 (12) |
| O3A—C2A—C3A—C4A | 0.66 (19) | C3C—C4C—C7C—C10C | 87.30 (11) |
| O1A—C2A—C3A—C4A | −179.62 (11) | C5C—C4C—C7C—C8C | 30.61 (13) |
| C2A—C3A—C4A—C5A | −2.4 (2) | C3C—C4C—C7C—C8C | −150.91 (9) |
| O2A—C5A—C4A—C3A | −176.96 (12) | C9C—C10C—C7C—O1C | −62.30 (10) |
| O4A—C5A—C4A—C3A | 2.41 (19) | C9C—C10C—C7C—C4C | 178.59 (8) |
| C2C—C1C—C6C—C5C | 0.00 (16) | C9C—C10C—C7C—C8C | 55.07 (11) |
| Cl1—C1C—C6C—C5C | −179.61 (8) | C11C—C8C—C7C—O1C | 60.01 (11) |

| | | | |
|---|---|---|---|
| C1C—C6C—C5C—C4C | −0.44 (16) | C11C—C8C—C7C—C4C | −176.97 (8) |
| C3C—C4C—C5C—C6C | 0.87 (15) | C11C—C8C—C7C—C10C | −54.84 (11) |
| C7C—C4C—C5C—C6C | 179.36 (9) | C7C—C10C—C9C—N1C | −56.43 (11) |
| C5C—C4C—C3C—C2C | −0.88 (16) | C7C—C8C—C11C—N1C | 56.71 (11) |
| C7C—C4C—C3C—C2C | −179.42 (9) | C8C—C11C—N1C—C9C | −58.48 (11) |
| C6C—C1C—C2C—C3C | 0.00 (16) | C10C—C9C—N1C—C11C | 57.97 (11) |

*Hydrogen-bond geometry (Å, °)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| O1C—H1C···O2B$^{i}$ | 0.82 | 1.97 | 2.7852 (13) | 171. |
| O1A—H2A···O1B$^{ii}$ | 0.90 (2) | 1.68 (2) | 2.5546 (13) | 162 (2) |
| N1C—H13C···O3B$^{iii}$ | 0.890 (17) | 1.954 (18) | 2.8328 (14) | 168.6 (16) |
| N1C—H14C···O2A$^{iv}$ | 0.887 (17) | 2.087 (17) | 2.9144 (15) | 154.9 (15) |
| O4A—H1A···O3A | 0.91 (2) | 1.65 (2) | 2.5531 (13) | 173.7 (19) |
| O3B—H1B···O4B | 1.18 (2) | 1.23 (2) | 2.4108 (12) | 177 (2) |

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

***Table 2***

*Cg···Cg interactions (Å)*

Cg2 is the centroid of the C1–C6 ring.

| *CgX*···*CgY* | Cg···Cg | *CgX*···Perp | *CgY*···Perp |
|---|---|---|---|
| Cg2···Cg2$^{i}$ | 3.646 (5) | -3.460 (6) | -3.460 (6) |

Symmetry code: (i) -x ,y, 1/2-z.

**Fig. 1**

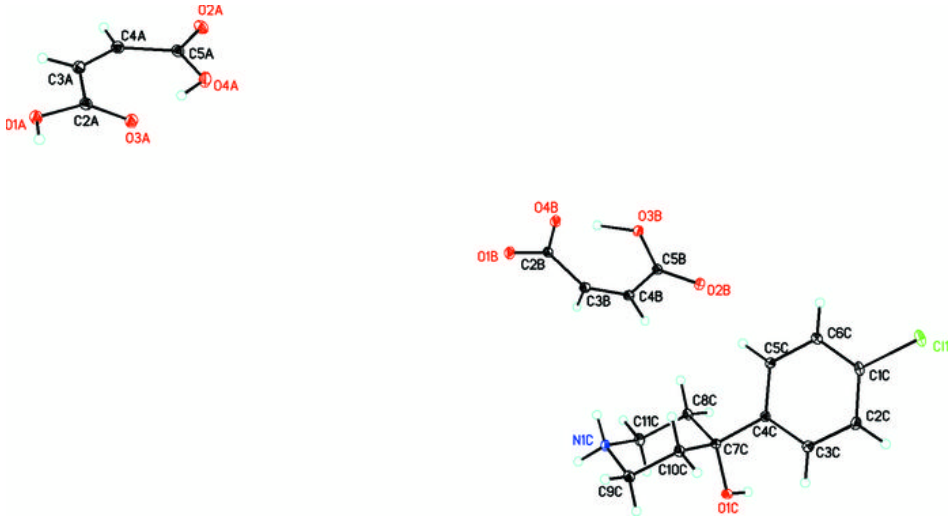
O2A
C4A
C5A
C3A
O4A
O1A
C2A
O3A
O4B
O3B
O1B
C2B
C5B
C3B
C4B
O2B
C6C
Cl1
C5C
C1C
C8C
C11C
C2C
N1C
C4C
C7C
C3C
C10C
C9C
O1C

**Fig. 2**