

Acta Crystallographica Section E

Structure Reports

Online

ISSN 1600-5368

4,8-Dihydroxy-2-methyl-1,2,3,4-tetrahydroisoquinolinium chloride monohydrate

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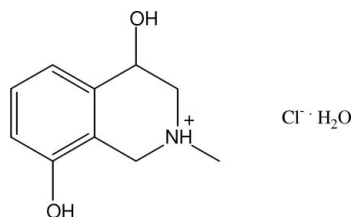
Received 20 April 2007; accepted 3 May 2007

Key indicators: single-crystal X-ray study; $T = 173$ K; mean $\sigma(\text{C}-\text{C}) = 0.002$ Å; R factor = 0.030; wR factor = 0.079; data-to-parameter ratio = 16.4.

Geometric parameters of the title compound, $\text{C}_{10}\text{H}_{14}\text{NO}_2^+\cdot\text{Cl}^-\cdot\text{H}_2\text{O}$, are in the usual ranges. The tetrahydropyridine ring adopts a half-chair conformation with the methyl group in an equatorial and the hydroxy group in an axial position. The crystal packing is stabilized by $\text{O}-\text{H}\cdots\text{O}$, $\text{O}-\text{H}\cdots\text{Cl}$ and $\text{N}-\text{H}\cdots\text{Cl}$ hydrogen bonds. The absolute configurations of both chiral centres have been determined to be R .

Related literature

For related literature, see: Ammon & Wheeler (1974), Ribár *et al.* (1991), Kametani & Fukumoto (1975), Croisy-Delcey *et al.* (1988) and Stambach *et al.* (1993).



Experimental

Crystal data

$\text{C}_{10}\text{H}_{14}\text{NO}_2^+\cdot\text{Cl}^-\cdot\text{H}_2\text{O}$
 $M_r = 233.69$
 Orthorhombic, $P2_12_12_1$
 $a = 7.3919$ (7) Å
 $b = 7.4823$ (7) Å
 $c = 20.4655$ (17) Å
 $V = 1131.91$ (18) Å³
 $Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 0.33$ mm⁻¹
 $T = 173$ (2) K
 $0.49 \times 0.48 \times 0.45$ mm

Data collection

Stoe IPDSII two-circle diffractometer
 Absorption correction: multi-scan (*MULABS*; Spek, 2003; Blessing, 1995)
 $T_{\min} = 0.857$, $T_{\max} = 0.868$
 6824 measured reflections
 2586 independent reflections
 2490 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.042$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.030$
 $wR(F^2) = 0.079$
 $S = 1.07$
 2586 reflections
 158 parameters
 H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\text{max}} = 0.23$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.18$ e Å⁻³
 Absolute structure: Flack (1983), 1057 Friedel pairs
 Flack parameter: 0.02 (6)

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{O1W}-\text{H1WA}\cdots\text{O31}^i$	0.88 (3)	1.93 (3)	2.7733 (17)	161 (2)
$\text{N1}-\text{H1}\cdots\text{Cl1}$	0.94 (2)	2.25 (2)	3.1204 (13)	153.6 (17)
$\text{O31}-\text{H31}\cdots\text{Cl1}^{ii}$	0.79 (2)	2.28 (2)	3.0682 (12)	177 (2)
$\text{O71}-\text{H71}\cdots\text{O1W}$	0.90 (3)	1.79 (3)	2.6803 (17)	174 (2)
$\text{O1W}-\text{H1WB}\cdots\text{Cl1}^i$	0.89 (3)	2.26 (3)	3.1299 (14)	165 (3)

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

Data collection: *X-Area* (Stoe & Cie, 2001); cell refinement: *X-Area*; data reduction: *X-Area*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97*.

ANM thanks the University of Mysore for permission to carry out the research work and Sequent Scientific Ltd., Mangalore, for a sample of the starting material for this synthesis.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: PV2011).

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supplementary materials

Acta Cryst. (2007). E63, o2885 [doi:10.1107/S1600536807022003]

4,8-Dihydroxy-2-methyl-1,2,3,4-tetrahydroisoquinolinium chloride monohydrate

H. S. Yathirajan, A. N. Mayekar, B. K. Sarojini, B. Narayana and M. Bolte

Comment

Synthesis of hydroxyl containing derivatives of tetrahydroisoquinolines are of interest as potential biologically active and medicinal substances. Aminoalkylamino derivatives of dihydroxy-benzoisoquinoline dione and of trihydroxy-naphtho[2,3-g]isoquinoline dione are biologically interesting molecules and synthesis and anti-tumor evaluation of these compounds are reported. 2-(Aminobenzyl)-1,2,3,4-tetrahydroisoquinolines are a new class of α 2-adrenergic receptor antagonists. A new derivative of tetrahydroderivative of isoquinoline hydrochloride, $C_{10}H_{14}NO_2^+Cl^- \cdot H_2O$, was prepared and its crystal structure was determined. Geometric parameters of the title compound are in the usual ranges. The tetrahydropyridine ring adopts a half chair conformation with the methyl group in an equatorial and the hydroxy group in an axial position. The crystal packing is stabilized by $OH \cdots O$, $OH \cdots Cl$ and $NH \cdots Cl$ hydrogen bonds.

Experimental

L-Phenylephrine.hydrochloride (10 g, 0.05 mol) was taken in 25 ml of water and stirred for 10 min. by adjusting the pH to 7 using 1 N sodium bicarbonate solution. 4 g of formaldehyde was added to the above mixture and stirred for 3 days. The reaction mass was concentrated to residue. Acetone/ethylacetate mixture was added and filtered. The filtrate was allowed to evaporate. The crystals were obtained from a 1:1 mixture of acetone and toluene (m.p.: 507-509 K).

Refinement

H atoms were found in a difference map, but those bonded to C were refined using a riding model with C—H ranging from 0.95 Å to 1.00 Å and $U_{iso}(H) = 1.2U_{eq}(C)$ or $U_{iso}(H) = 1.5U_{eq}(C_{methyl})$. The methyl group was allowed to rotate but not to tip. H atoms bonded to N and O were freely refined.

Figures

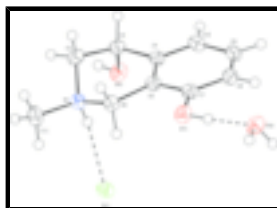


Fig. 1. Perspective view of the title compound with the atom numbering; displacement ellipsoids are at the 50% probability level.

4,8-Dihydroxy-2-methyl-1,2,3,4-tetrahydroisoquinolinium chloride monohydrate

Crystal data

$C_{10}H_{14}NO_2^+ \cdot Cl^- \cdot H_2O$

$F_{000} = 496$

supplementary materials

$M_r = 233.69$

Orthorhombic, $P2_12_12_1$

Hall symbol: P 2ac 2ab

$a = 7.3919$ (7) Å

$b = 7.4823$ (7) Å

$c = 20.4655$ (17) Å

$V = 1131.91$ (18) Å³

$Z = 4$

$D_x = 1.371$ Mg m⁻³

Mo $K\alpha$ radiation

$\lambda = 0.71073$ Å

Cell parameters from 5354 reflections

$\theta = 3.1$ – 27.2°

$\mu = 0.33$ mm⁻¹

$T = 173$ (2) K

Block, colourless

$0.49 \times 0.48 \times 0.45$ mm

Data collection

Stoe IPDSII two-circle diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 173$ (2) K

ω scans

Absorption correction: multi-scan (MULABS; Spek, 2003; Blessing, 1995)

$T_{\min} = 0.857$, $T_{\max} = 0.868$

6824 measured reflections

2586 independent reflections

2490 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.042$

$\theta_{\text{max}} = 27.5^\circ$

$\theta_{\text{min}} = 2.9^\circ$

$h = -9 \rightarrow 8$

$k = -9 \rightarrow 9$

$l = -20 \rightarrow 26$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.030$

$wR(F^2) = 0.079$

$S = 1.07$

2586 reflections

158 parameters

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

$w = 1/[\sigma^2(F_o^2) + (0.0479P)^2 + 0.1411P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}} < 0.001$

$\Delta\rho_{\text{max}} = 0.23$ e Å⁻³

$\Delta\rho_{\text{min}} = -0.18$ e Å⁻³

Extinction correction: SHELXL97,

$F_c^* = kF_c[1 + 0.001xF_c^2\lambda^3/\sin(2\theta)]^{-1/4}$

Extinction coefficient: 0.068 (5)

Absolute structure: Flack (1983), 1057 Friedel pairs

Flack parameter: 0.02 (6)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds 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 $F^2 > 2\sigma(F^2)$ 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)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
N1	0.27972 (17)	0.63969 (16)	0.34303 (6)	0.0225 (3)
H1	0.306 (3)	0.526 (3)	0.3266 (10)	0.031 (5)*
C2	0.4382 (2)	0.7638 (2)	0.34089 (7)	0.0252 (3)
H2A	0.4121	0.8719	0.3672	0.030*
H2B	0.4611	0.8015	0.2953	0.030*
C3	0.6041 (2)	0.66956 (18)	0.36796 (7)	0.0225 (3)
H3	0.7030	0.7592	0.3741	0.027*
C4	0.5654 (2)	0.57941 (19)	0.43313 (7)	0.0219 (3)
C5	0.3868 (2)	0.55552 (18)	0.45376 (7)	0.0213 (3)
C6	0.2252 (2)	0.60402 (19)	0.41250 (7)	0.0223 (3)
H6A	0.1365	0.5050	0.4136	0.027*
H6B	0.1663	0.7117	0.4308	0.027*
C7	0.3526 (2)	0.47986 (19)	0.51550 (7)	0.0230 (3)
C8	0.4951 (2)	0.4193 (2)	0.55410 (8)	0.0264 (3)
H8	0.4719	0.3663	0.5954	0.032*
C9	0.6720 (2)	0.4370 (2)	0.53162 (7)	0.0267 (3)
H9	0.7691	0.3924	0.5573	0.032*
C10	0.7083 (2)	0.5193 (2)	0.47190 (7)	0.0259 (3)
H10	0.8297	0.5343	0.4577	0.031*
C11	0.1222 (2)	0.7095 (2)	0.30450 (8)	0.0329 (3)
H11A	0.0183	0.6297	0.3103	0.049*
H11B	0.1547	0.7148	0.2581	0.049*
H11C	0.0908	0.8295	0.3199	0.049*
O31	0.66470 (15)	0.53406 (15)	0.32328 (6)	0.0266 (3)
H31	0.689 (3)	0.585 (3)	0.2903 (11)	0.036 (6)*
O71	0.17572 (16)	0.46923 (16)	0.53358 (6)	0.0288 (3)
H71	0.164 (4)	0.416 (3)	0.5726 (14)	0.055 (7)*
Cl1	0.23462 (5)	0.24143 (5)	0.300840 (16)	0.02720 (12)
O1W	0.13199 (19)	0.32949 (16)	0.65313 (6)	0.0327 (3)
H1WA	0.158 (4)	0.215 (3)	0.6527 (12)	0.048 (6)*
H1WB	0.014 (4)	0.328 (4)	0.6626 (13)	0.059 (8)*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0220 (6)	0.0246 (6)	0.0208 (6)	0.0007 (5)	-0.0004 (5)	0.0000 (4)
C2	0.0270 (7)	0.0229 (6)	0.0258 (6)	-0.0009 (6)	0.0040 (5)	0.0023 (6)
C3	0.0227 (7)	0.0214 (6)	0.0235 (7)	-0.0017 (6)	0.0035 (6)	-0.0011 (5)
C4	0.0243 (7)	0.0224 (6)	0.0191 (6)	-0.0011 (5)	0.0001 (5)	-0.0024 (5)

supplementary materials

C5	0.0230 (7)	0.0209 (6)	0.0201 (6)	-0.0006 (6)	0.0009 (5)	-0.0017 (5)
C6	0.0199 (6)	0.0260 (6)	0.0210 (6)	0.0001 (5)	0.0023 (5)	0.0005 (5)
C7	0.0258 (7)	0.0224 (6)	0.0207 (6)	-0.0007 (5)	0.0019 (6)	-0.0023 (5)
C8	0.0342 (8)	0.0244 (7)	0.0207 (6)	0.0003 (6)	-0.0014 (6)	-0.0009 (5)
C9	0.0280 (7)	0.0281 (7)	0.0238 (7)	0.0017 (6)	-0.0066 (6)	-0.0016 (6)
C10	0.0218 (7)	0.0312 (7)	0.0248 (7)	-0.0020 (6)	-0.0009 (6)	-0.0039 (6)
C11	0.0265 (7)	0.0426 (8)	0.0295 (7)	0.0063 (6)	-0.0046 (6)	0.0075 (7)
O31	0.0311 (6)	0.0263 (5)	0.0222 (5)	0.0014 (5)	0.0081 (5)	0.0011 (4)
O71	0.0274 (6)	0.0329 (6)	0.0262 (5)	-0.0015 (5)	0.0054 (5)	0.0039 (5)
Cl1	0.02922 (18)	0.02989 (18)	0.02250 (17)	-0.00307 (15)	0.00038 (13)	-0.00474 (13)
O1W	0.0373 (7)	0.0282 (6)	0.0325 (6)	-0.0009 (5)	0.0079 (5)	0.0043 (5)

Geometric parameters (\AA , $^\circ$)

N1—C2	1.4957 (19)	C6—H6B	0.9900
N1—C11	1.500 (2)	C7—O71	1.3611 (19)
N1—C6	1.5017 (18)	C7—C8	1.393 (2)
N1—H1	0.94 (2)	C8—C9	1.392 (2)
C2—C3	1.519 (2)	C8—H8	0.9500
C2—H2A	0.9900	C9—C10	1.395 (2)
C2—H2B	0.9900	C9—H9	0.9500
C3—O31	1.4369 (18)	C10—H10	0.9500
C3—C4	1.5218 (19)	C11—H11A	0.9800
C3—H3	1.0000	C11—H11B	0.9800
C4—C10	1.396 (2)	C11—H11C	0.9800
C4—C5	1.398 (2)	O31—H31	0.79 (2)
C5—C7	1.407 (2)	O71—H71	0.90 (3)
C5—C6	1.507 (2)	O1W—H1WA	0.88 (3)
C6—H6A	0.9900	O1W—H1WB	0.89 (3)
C2—N1—C11	112.12 (12)	C5—C6—H6A	109.4
C2—N1—C6	110.38 (11)	N1—C6—H6B	109.4
C11—N1—C6	110.57 (12)	C5—C6—H6B	109.4
C2—N1—H1	113.3 (13)	H6A—C6—H6B	108.0
C11—N1—H1	106.7 (13)	O71—C7—C8	123.60 (14)
C6—N1—H1	103.4 (12)	O71—C7—C5	116.10 (14)
N1—C2—C3	109.47 (11)	C8—C7—C5	120.29 (14)
N1—C2—H2A	109.8	C9—C8—C7	119.47 (14)
C3—C2—H2A	109.8	C9—C8—H8	120.3
N1—C2—H2B	109.8	C7—C8—H8	120.3
C3—C2—H2B	109.8	C8—C9—C10	120.83 (14)
H2A—C2—H2B	108.2	C8—C9—H9	119.6
O31—C3—C2	110.32 (12)	C10—C9—H9	119.6
O31—C3—C4	107.67 (11)	C9—C10—C4	119.65 (14)
C2—C3—C4	111.96 (12)	C9—C10—H10	120.2
O31—C3—H3	108.9	C4—C10—H10	120.2
C2—C3—H3	108.9	N1—C11—H11A	109.5
C4—C3—H3	108.9	N1—C11—H11B	109.5
C10—C4—C5	120.15 (13)	H11A—C11—H11B	109.5
C10—C4—C3	119.93 (13)	N1—C11—H11C	109.5

C5—C4—C3	119.92 (13)	H11A—C11—H11C	109.5
C4—C5—C7	119.48 (13)	H11B—C11—H11C	109.5
C4—C5—C6	123.27 (12)	C3—O31—H31	105.8 (16)
C7—C5—C6	117.24 (13)	C7—O71—H71	111.2 (18)
N1—C6—C5	111.15 (12)	H1WA—O1W—H1WB	102 (3)
N1—C6—H6A	109.4		
C11—N1—C2—C3	-167.99 (12)	C11—N1—C6—C5	-173.04 (12)
C6—N1—C2—C3	68.26 (15)	C4—C5—C6—N1	12.93 (18)
N1—C2—C3—O31	70.79 (15)	C7—C5—C6—N1	-165.99 (12)
N1—C2—C3—C4	-49.10 (16)	C4—C5—C7—O71	176.75 (13)
O31—C3—C4—C10	72.13 (16)	C6—C5—C7—O71	-4.29 (19)
C2—C3—C4—C10	-166.44 (13)	C4—C5—C7—C8	-3.9 (2)
O31—C3—C4—C5	-107.27 (15)	C6—C5—C7—C8	175.06 (13)
C2—C3—C4—C5	14.16 (18)	O71—C7—C8—C9	-179.57 (15)
C10—C4—C5—C7	3.7 (2)	C5—C7—C8—C9	1.1 (2)
C3—C4—C5—C7	-176.94 (12)	C7—C8—C9—C10	1.9 (2)
C10—C4—C5—C6	-175.23 (14)	C8—C9—C10—C4	-2.1 (2)
C3—C4—C5—C6	4.2 (2)	C5—C4—C10—C9	-0.7 (2)
C2—N1—C6—C5	-48.40 (15)	C3—C4—C10—C9	179.92 (13)

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

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
O1W—H1WA \cdots O31 ⁱ	0.88 (3)	1.93 (3)	2.7733 (17)	161 (2)
N1—H1 \cdots C11	0.94 (2)	2.25 (2)	3.1204 (13)	153.6 (17)
O31—H31 \cdots C11 ⁱⁱ	0.79 (2)	2.28 (2)	3.0682 (12)	177 (2)
O71—H71 \cdots O1W	0.90 (3)	1.79 (3)	2.6803 (17)	174 (2)
O1W—H1WB \cdots C11 ⁱ	0.89 (3)	2.26 (3)	3.1299 (14)	165 (3)

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

Fig. 1

