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

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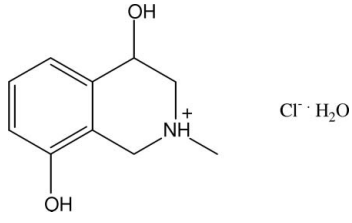
Key indicators: single-crystal X-ray study; T = 173 K; mean σ(C–C) = 0.002 Å; R factor = 0.030; wR factor = 0.079; data-to-parameter ratio = 16.4.

Geometric parameters of the title compound, $C_{10}H_{14}NO_2^+\cdot Cl^-\cdot H_2O$, 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 O—H···O, O—H···Cl and N—H···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

$C_{10}H_{14}NO_2^+\cdot Cl^-\cdot H_2O$
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) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.33 mm^{-1}
T = 173 (2) K
0.49 × 0.48 × 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_{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
$\Delta\rho_{max}$ = 0.23 e Å^{-3}
$\Delta\rho_{min}$ = −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···A	D—H	H···A	D···A	D—H···A
O1W—H1WA···O31^{i}	0.88 (3)	1.93 (3)	2.7733 (17)	161 (2)
N1—H1···Cl1	0.94 (2)	2.25 (2)	3.1204 (13)	153.6 (17)
O31—H31···Cl1^{ii}	0.79 (2)	2.28 (2)	3.0682 (12)	177 (2)
O71—H71···O1W	0.90 (3)	1.79 (3)	2.6803 (17)	174 (2)
O1W—H1WB···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

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

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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 α2-adrenergic receptor antagonists. A new derivative of tetrahydroderivative of isoquinoline hydrochloride, $C_{10}H_{14}NO_2^+Cl^-.H_2O$, 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···O, OH···Cl and NH···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 yo 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 0.95Å to 1.00Å 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

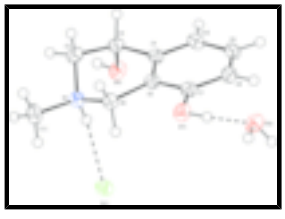

Fig. 1. Perspective view of the title compound with the atom numbering; displacement ellipsoids are at the 50% probability level.

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

Crystal data

$C_{10}H_{14}NO_2^+\cdot Cl^-\cdot H_2O$ $F_{000} = 496$

M_r = 233.69	D_x = 1.371 Mg m^{-3}
Orthorhombic, $P2_12_12_1$	Mo $K\alpha$ radiation λ = 0.71073 Å
Hall symbol: P 2ac 2ab	Cell parameters from 5354 reflections
a = 7.3919 (7) Å	θ = 3.1–27.2º
b = 7.4823 (7) Å	μ = 0.33 mm^{-1}
c = 20.4655 (17) Å	T = 173 (2) K
V = 1131.91 (18) Å^3	Block, colourless
Z = 4	0.49 × 0.48 × 0.45 mm

Data collection

Stoe IPDSII two-circle diffractometer	2586 independent reflections
Radiation source: fine-focus sealed tube	2490 reflections with $I > 2\sigma(I)$
Monochromator: graphite	R_{int} = 0.042
T = 173(2) K	θ_{max} = 27.5º
ω scans	θ_{min} = 2.9º
Absorption correction: multi-scan (MULABS; Spek, 2003; Blessing, 1995)	h = −9→8
T_{min} = 0.857, T_{max} = 0.868	k = −9→9
6824 measured reflections	l = −20→26

Refinement

Refinement on F^2	H atoms treated by a mixture of independent and constrained refinement
Least-squares matrix: full	$w = 1/[\sigma^2(F_o^2) + (0.0479P)^2 + 0.1411P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)]$ = 0.030	$(\Delta/\sigma)_{max} < 0.001$
$wR(F^2)$ = 0.079	$\Delta\rho_{max}$ = 0.23 e Å^{-3}
S = 1.07	$\Delta\rho_{min}$ = −0.18 e Å^{-3}
2586 reflections	Extinction correction: SHELXL97, $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
158 parameters	Extinction coefficient: 0.068 (5)
Primary atom site location: structure-invariant direct methods	Absolute structure: Flack (1983), 1057 Friedel pairs
Secondary atom site location: difference Fourier map	Flack parameter: 0.02 (6)
Hydrogen site location: inferred from neighbouring sites	

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 $F^2 > 2\text{sigma}(F^2)$ 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}
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 (Å^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)

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 (Å, °)

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 (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1W—H1WA···O31^{i}	0.88 (3)	1.93 (3)	2.7733 (17)	161 (2)
N1—H1···Cl1	0.94 (2)	2.25 (2)	3.1204 (13)	153.6 (17)
O31—H31···Cl1^{ii}	0.79 (2)	2.28 (2)	3.0682 (12)	177 (2)
O71—H71···O1W	0.90 (3)	1.79 (3)	2.6803 (17)	174 (2)
O1W—H1WB···Cl1^{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