organic compounds

4-Hydroxy-2,2,6,6-tetramethyl-piperidinium nitrate

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Anions and cations of the title compound, $C_9H_{20}NO^+\cdot NO_3^-$, are located on crystallographic mirror planes. The six-membered ring adopts a chair conformation with the hydroxyl group in an equatorial position. Intermolecular hydrogen bonds connect anions and cations.

Related literature

For general background, see: Borzatta & Carrozza (1991). For a related structure, see: Nengfang et al. (2005).
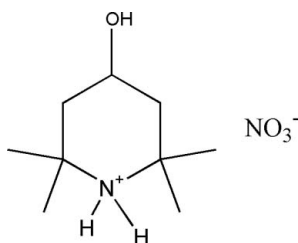
Experimental

Crystal data

$C_9H_{20}NO^+\cdot NO_3^-$
$M_r = 220.27$
Orthorhombic, $Cmc2_1$

$a = 11.6721$ (15) Å
$b = 10.5156$ (12) Å
$c = 9.6565$ (12) Å

$V = 1185.2$ (3) Å^3
$Z = 4$
Mo $K\alpha$ radiation

$\mu = 0.10$ mm^{-1}
$T = 113$ (2) K
$0.24 \times 0.12 \times 0.10$ mm

Data collection

Rigaku Saturn diffractometer
Absorption correction: multi-scan (CrystalClear; Rigaku/MSC, 2005)
$T_{min} = 0.977$, $T_{max} = 0.990$

5449 measured reflections
789 independent reflections
742 reflections with $I > 2\sigma(I)$
$R_{int} = 0.059$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.047$
$wR(F^2) = 0.115$
$S = 1.11$
789 reflections
92 parameters
1 restraint

H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max} = 0.21$ e Å^{-3}
$\Delta\rho_{min} = -0.16$ e Å^{-3}

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O1—H1$\cdots$O4^i	0.92 (6)	2.61 (5)	3.279 (4)	129 (4)
O1—H1$\cdots$N2^i	0.92 (6)	2.57 (6)	3.438 (4)	157 (5)
O1—H1$\cdots$O3^i	0.92 (6)	1.84 (7)	2.760 (4)	175 (5)
N1—H1$B\cdots$N2^{ii}	0.96 (5)	2.54 (5)	3.444 (4)	157 (3)
N1—H1$B\cdots$O3^{ii}	0.96 (5)	2.44 (5)	3.118 (4)	128 (3)
N1—H1$B\cdots$O2^{ii}	0.96 (5)	1.92 (5)	2.882 (4)	175 (4)
N1—H1$A\cdots$O1^{iii}	0.93 (5)	1.99 (5)	2.909 (4)	171 (4)

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) $x, -y, z - \frac{1}{2}$.

Data collection: CrystalClear (Rigaku/MSC, 2005); cell refinement: CrystalClear; data reduction: CrystalClear; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: SHELXTL (Bruker, 1997); software used to prepare material for publication: SHELXTL.

References

Borzatta, V. & Carrozza, P. (1991). European Patent EP 0 462 069.

Bruker (1997). SHELXTL. Bruker AXS Inc., Madison, Wisconsin, USA.

Nengfang, S., Guo, H. Z., Yin, G. D. & Wu, A. X. (2005). Acta Cryst. E61, o2902–o2903.

Rigaku/MSC (2005). CrystalClear and CrystalStructure. Rigaku/MSC, The Woodlands, Texas, USA .

Sheldrick, G. M. (1997). SHELXS97 and SHELXL97. University of Göttingen, Germany.

supplementary materials

4-Hydroxy-2,2,6,6-tetramethylpiperidinium nitrate

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Comment

2,2,6,6-tetramethylpiperidin-4-ol is a very important intermediate in the synthesis of light stabilizers (Borzatta & Carrozza, 1991).

Anions and cations of the title compound, $C_9H_{19}NO^+ \cdot HNO_3^-$, are located on crystallographic mirror planes. The six-membered ring adopts a chair conformation with the hydroxyl group in an equatorial position. Intermolecular hydrogen bonds connect anions and cations.

Experimental

An ethanol solution(10 ml) of 2,2,6,6-tetramethylpiperidin-4-ol (3.2 mmol,0.5 g) was added dropwise to a stirred aqueous solution (6 ml) of nitric acid (4.5 mmol,0.28 g) at 293 K. Then, the reaction mixture was filtered and the filtrate stood for about five days until yellow needle shaped crystals were obtained.

Refinement

All H atoms bonded to C were positioned geometrically (C—H ranging from 0.98 to 1.00 Å) and refined as riding with $U_{iso}(H)=1.2U_{eq}(C)$ or $1.5_{eq}(C)$ for methyl groups. H atoms bonded to N and O were freely refined.
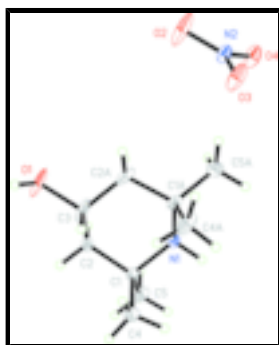
Figures

Fig. 1. A perspective view of the title compound. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

4-Hydroxy-2,2,6,6-tetramethylpiperidinium nitrate

Crystal data

$C_9H_{20}NO^+ \cdot NO_3^-$	$D_x = 1.234$ Mg m^{-3}
$M_r = 220.27$	Mo $K\alpha$ radiation

Orthorhombic, $Cmc2_1$

$a = 11.6721\ (15)$ Å

$b = 10.5156\ (12)$ Å

$c = 9.6565\ (12)$ Å

$V = 1185.2\ (3)$ Å^3

$Z = 4$

$F_{000} = 480$

$\lambda = 0.71070$ Å

Cell parameters from 1339 reflections

$\theta = 2.6–28.0º$

$\mu = 0.10$ mm^{-1}

$T = 113\ (2)$ K

Prism, colorless

$0.24 \times 0.12 \times 0.10$ mm

Data collection

Rigaku Saturn diffractometer

Radiation source: rotating anode

Monochromator: confocal

$T = 113(2)$ K

ω scans

Absorption correction: multi-scan (CrystalClear; Rigaku/MSC, 2005)

$T_{min} = 0.977$, $T_{max} = 0.990$

5449 measured reflections

789 independent reflections

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

$R_{int} = 0.059$

$\theta_{max} = 27.9º$

$\theta_{min} = 2.6º$

$h = -15 \rightarrow 15$

$k = -13 \rightarrow 13$

$l = -12 \rightarrow 12$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.047$

$wR(F^2) = 0.115$

$S = 1.11$

789 reflections

92 parameters

1 restraint

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

$w = 1/[\sigma^2(F_o^2) + (0.0568P)^2 + 0.4524P]$
where $P = (F_o^2 + 2F_c^2)/3$

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

$\Delta\rho_{max} = 0.21$ e Å^{-3}

$\Delta\rho_{min} = -0.16$ e Å^{-3}

Extinction correction: SHELXL, $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$

Extinction coefficient: 0.010 (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 > 2sigma(F^2) is used only for calculat-

ing *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*	$U_{iso}*/U_{eq}$
O2	0.0000	0.1257 (3)	0.3803 (3)	0.0692 (13)
O3	0.0000	0.3084 (2)	0.2792 (3)	0.0505 (9)
O4	0.0000	0.1368 (3)	0.1545 (3)	0.0402 (7)
N1	0.5000	0.1910 (3)	0.1021 (3)	0.0199 (6)
H1A	0.5000	0.109 (4)	0.067 (5)	0.033 (12)*
H1B	0.5000	0.248 (4)	0.024 (5)	0.032 (10)*
N2	0.0000	0.1891 (3)	0.2702 (3)	0.0271 (7)
C1	0.6143 (2)	0.2061 (2)	0.1790 (3)	0.0275 (6)
C2	0.6069 (2)	0.1267 (3)	0.3139 (3)	0.0342 (7)
H2A	0.6073	0.0352	0.2897	0.041*
H2B	0.6756	0.1438	0.3709	0.041*
C3	0.5000	0.1555 (4)	0.3994 (4)	0.0434 (12)
H3	0.5000	0.2471	0.4271	0.052*
C4	0.6395 (3)	0.3482 (3)	0.2066 (4)	0.0448 (8)
H4A	0.7192	0.3580	0.2366	0.067*
H4B	0.5881	0.3796	0.2793	0.067*
H4C	0.6270	0.3970	0.1215	0.067*
C5	0.7050 (3)	0.1520 (3)	0.0804 (4)	0.0524 (10)
H5A	0.6875	0.0627	0.0604	0.079*
H5B	0.7807	0.1579	0.1238	0.079*
H5C	0.7048	0.2008	−0.0061	0.079*
H1	0.5000	0.119 (5)	0.606 (7)	0.050 (14)*
O1	0.5000	0.0759 (3)	0.5227 (3)	0.0644 (13)

Atomic displacement parameters ($Å^2$)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O2	0.167 (4)	0.0233 (15)	0.0174 (15)	0.000	0.000	0.0026 (13)
O3	0.110 (3)	0.0174 (14)	0.0243 (14)	0.000	0.000	0.0001 (12)
O4	0.072 (2)	0.0291 (14)	0.0190 (13)	0.000	0.000	−0.0056 (11)
N1	0.0273 (14)	0.0164 (13)	0.0159 (14)	0.000	0.000	−0.0010 (11)
N2	0.0429 (18)	0.0201 (14)	0.0184 (15)	0.000	0.000	−0.0017 (13)
C1	0.0287 (12)	0.0236 (13)	0.0302 (13)	−0.0052 (9)	−0.0077 (10)	0.0105 (10)
C2	0.0498 (16)	0.0213 (12)	0.0314 (14)	−0.0100 (11)	−0.0204 (12)	0.0102 (10)
C3	0.103 (4)	0.0141 (17)	0.0133 (17)	0.000	0.000	0.0023 (14)
C4	0.0562 (16)	0.0321 (16)	0.0462 (17)	−0.0199 (13)	−0.0209 (15)	0.0165 (13)
C5	0.0362 (16)	0.0447 (19)	0.076 (3)	0.0095 (13)	0.0158 (17)	0.0283 (18)
O1	0.164 (4)	0.0192 (14)	0.0104 (14)	0.000	0.000	0.0019 (12)

Geometric parameters (Å, °)

O2—N2	1.254 (4)	C2—H2B	0.9900

O3—N2	1.258 (4)	C3—O1	1.455 (4)
O4—N2	1.245 (4)	C3—C2^i	1.527 (4)
N1—C1	1.534 (3)	C3—H3	1.0000
N1—C1^i	1.534 (3)	C4—H4A	0.9800
N1—H1A	0.93 (5)	C4—H4B	0.9800
N1—H1B	0.96 (5)	C4—H4C	0.9800
C1—C5	1.534 (4)	C5—H5A	0.9800
C1—C4	1.547 (4)	C5—H5B	0.9800
C1—C2	1.550 (4)	C5—H5C	0.9800
C2—C3	1.527 (4)	O1—H1	0.92 (6)
C2—H2A	0.9900		
C1—N1—C1^i	120.7 (3)	H2A—C2—H2B	107.8
C1—N1—H1A	105.9 (13)	O1—C3—C2^i	109.16 (19)
C1^i—N1—H1A	105.9 (13)	O1—C3—C2	109.16 (19)
C1—N1—H1B	108.4 (10)	C2^i—C3—C2	109.6 (3)
C1^i—N1—H1B	108.4 (10)	O1—C3—H3	109.6
H1A—N1—H1B	107 (4)	C2^i—C3—H3	109.6
O4—N2—O2	121.7 (3)	C2—C3—H3	109.6
O4—N2—O3	120.2 (3)	C1—C4—H4A	109.5
O2—N2—O3	118.1 (3)	C1—C4—H4B	109.5
C5—C1—N1	105.2 (2)	H4A—C4—H4B	109.5
C5—C1—C4	109.5 (2)	C1—C4—H4C	109.5
N1—C1—C4	110.4 (2)	H4A—C4—H4C	109.5
C5—C1—C2	111.1 (2)	H4B—C4—H4C	109.5
N1—C1—C2	107.6 (2)	C1—C5—H5A	109.5
C4—C1—C2	112.7 (2)	C1—C5—H5B	109.5
C3—C2—C1	113.2 (2)	H5A—C5—H5B	109.5
C3—C2—H2A	108.9	C1—C5—H5C	109.5
C1—C2—H2A	108.9	H5A—C5—H5C	109.5
C3—C2—H2B	108.9	H5B—C5—H5C	109.5
C1—C2—H2B	108.9	C3—O1—H1	116 (3)
C1^i—N1—C1—C5	166.0 (2)	N1—C1—C2—C3	−51.4 (3)
C1^i—N1—C1—C4	−75.9 (4)	C4—C1—C2—C3	70.6 (3)
C1^i—N1—C1—C2	47.5 (4)	C1—C2—C3—O1	179.4 (2)
C5—C1—C2—C3	−166.0 (2)	C1—C2—C3—C2^i	59.9 (3)

Symmetry codes: (i) −x+1, y, z.

Hydrogen-bond geometry (Å, °)

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
O1—H1⋯O4^{ii}	0.92 (6)	2.61 (5)	3.279 (4)	129 (4)
O1—H1⋯N2^{ii}	0.92 (6)	2.57 (6)	3.438 (4)	157 (5)
O1—H1⋯O3^{ii}	0.92 (6)	1.84 (7)	2.760 (4)	175 (5)
N1—H1B⋯N2^{iii}	0.96 (5)	2.54 (5)	3.444 (4)	157 (3)
N1—H1B⋯O3^{iii}	0.96 (5)	2.44 (5)	3.118 (4)	128 (3)

N1—H1B···O2^{iii}	0.96 (5)	1.92 (5)	2.882 (4)	175 (4)
N1—H1A···O1^{iv}	0.93 (5)	1.99 (5)	2.909 (4)	171 (4)

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

Fig. 1