

Acta Crystallographica Section E

Structure Reports

Online

ISSN 1600-5368

4-Hydroxy-2,2,6,6-tetramethylpiperidinium hydrogensulfate monohydrate

Li Xiao,^a Yun-Hui Zhang,^a Ying Cui,^a Xing-Hua Jin^a and Wei Wang^{b*}

^aCollege of Pharmaceuticals and Biotechnology, Tianjin University, Tianjin 300072, People's Republic of China, and ^bSchool of Chemical Engineering, University of Science and Technology, Liaoning, Anshan 114051, People's Republic of China
Correspondence e-mail: tju_chemistry@yahoo.com.cn

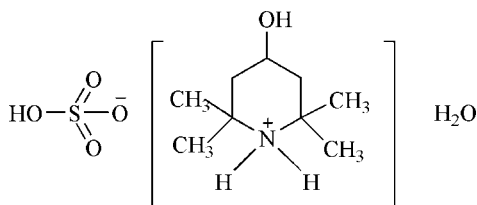
Received 12 December 2007; accepted 19 December 2007

Key indicators: single-crystal X-ray study; $T = 294$ K; mean $\sigma(\text{C}-\text{C}) = 0.004$ Å; R factor = 0.040; wR factor = 0.108; data-to-parameter ratio = 13.5.

In the title compound, $\text{C}_9\text{H}_{20}\text{NO}^+\cdot\text{HO}_4\text{S}^-\cdot\text{H}_2\text{O}$, the piperidinium ring adopts a chair conformation. Intermolecular $\text{O}-\text{H}\cdots\text{O}$ and $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds form an extensive three-dimensional network, which consolidates the crystal structure.

Related literature

For useful applications of tetramethylpiperidinol, see: Gray (1991); Liu *et al.* (2006).



Experimental

Crystal data

$\text{C}_9\text{H}_{20}\text{NO}^+\cdot\text{HO}_4\text{S}^-\cdot\text{H}_2\text{O}$ $a = 8.334$ (3) Å
 $M_r = 273.34$ $b = 8.518$ (3) Å
 Triclinic, $P\bar{1}$ $c = 10.245$ (3) Å

$\alpha = 78.465$ (5)°
 $\beta = 82.546$ (5)°
 $\gamma = 71.586$ (4)°
 $V = 674.3$ (3) Å³
 $Z = 2$

Mo $K\alpha$ radiation
 $\mu = 0.26$ mm⁻¹
 $T = 294$ (2) K
 $0.26 \times 0.24 \times 0.20$ mm

Data collection

Bruker SMART CCD area-detector diffractometer 3506 measured reflections
 2374 independent reflections
 Absorption correction: multi-scan (SADABS; Bruker, 1997) 1929 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.016$
 $T_{\text{min}} = 0.936$, $T_{\text{max}} = 0.951$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.040$
 $wR(F^2) = 0.108$
 $S = 1.06$
 2374 reflections
 176 parameters
 5 restraints

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\text{max}} = 0.41$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.33$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{O2}-\text{H2}\cdots\text{O1}$	0.83 (2)	1.76 (2)	2.576 (3)	168 (4)
$\text{N1}-\text{H1A}\cdots\text{O5}^i$	0.86 (2)	1.933 (17)	2.795 (3)	178 (2)
$\text{N1}-\text{H1B}\cdots\text{O3}^{ii}$	0.86 (2)	2.154 (19)	3.002 (3)	168 (2)
$\text{O6}-\text{H6D}\cdots\text{O3}^{iii}$	0.82 (2)	2.06 (2)	2.874 (3)	169 (4)
$\text{O6}-\text{H6E}\cdots\text{O4}^{iv}$	0.81 (2)	2.00 (2)	2.790 (3)	165 (4)

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

Data collection: SMART (Bruker, 1997); cell refinement: SAINT (Bruker, 1997); data reduction: SAINT; 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.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: CV2376).

References

- Bruker (1997). SMART (Version 5.611), SAINT (Version 6.0), SADABS (Version 2.03) and SHELXTL (Version 5.10). Bruker AXS Inc., Madison, Wisconsin, USA.
 Gray, R. L. (1991). *Plast. Eng.* **47**, 21–23.
 Liu, X., Ju, C. X., Hu, R. S. & Gu, D. P. (2006). *J. Heibei Normal Univ. (Nat. Sci. Ed.)*, **30**, 326–328.
 Sheldrick, G. M. (1997). SHELXS97 and SHELXL97. University of Göttingen, Germany.

supplementary materials

Acta Cryst. (2008). E64, o350 [doi:10.1107/S1600536807067633]

4-Hydroxy-2,2,6,6-tetramethylpiperidinium hydrogensulfate monohydrate

L. Xiao, Y.-H. Zhang, Y. Cui, X.-H. Jin and W. Wang

Comment

Tetramethylpiperidinol is an important intermediate used in the synthesis of hindered amine light stabilizer (HALS) (Gray, 1991; Liu *et al.*, 2006). The title compound, (I), is a new derivative of tetramethylpiperidinol. Herein we report its crystal structure.

In (I) (Fig. 1), the piperidinium ring adopts a chair conformation. The hydroxy group attached at C1 is in equatorial position. In the crystal, the intermolecular O—H \cdots O and N—H \cdots O hydrogen bonds (Table 1) form an extensive three-dimensional network, which consolidates the packing.

Experimental

2,2,6,6-Tetramethylpiperidin-4-ol (40.0 g, 254 mmol) was dissolved in 98% H₂SO₄ (24.5 g) and then cooled to 278 K. With stirring, water (100 ml) was then added dropwise to the mixture over a period of 0.5 h. The mixture was stirred at 273–278 K for a further 3 h. The title compound (54.50 g) was obtained in powder form in a yield of 75.6%. Crystals of (I) were obtained by slow evaporation of a solution of water.

Refinement

H atoms attached to atoms N and O were located in a difference map and refined with bond restraints O—H = 0.82 (2) Å, N—H = 0.86 (2) Å. C-bound H atoms were positioned geometrically (C—H 0.96–0.98 Å). All H atoms were refined as riding, with $U_{\text{iso}}(\text{H})=1.2-1.5U_{\text{eq}}$ of the parent atom.

Figures

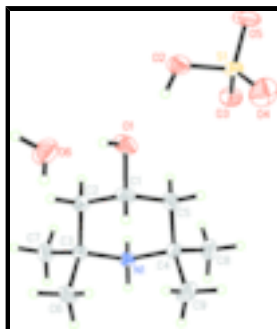


Fig. 1. The content of asymmetric unit of (I) with the atomic numbering and 35% probability displacement ellipsoids.

4-Hydroxy-2,2,6,6-tetramethylpiperidinium hydrogensulfate monohydrat

Crystal data

$C_9H_{20}NO^+ \cdot HO_4S^- \cdot H_2O$	$Z = 2$
$M_r = 273.34$	$F_{000} = 296$
Triclinic, $P\bar{1}$	$D_x = 1.346 \text{ Mg m}^{-3}$
Hall symbol: -P 1	Mo $K\alpha$ radiation
$a = 8.334 (3) \text{ \AA}$	$\lambda = 0.71073 \text{ \AA}$
$b = 8.518 (3) \text{ \AA}$	Cell parameters from 1816 reflections
$c = 10.245 (3) \text{ \AA}$	$\theta = 2.6\text{--}26.2^\circ$
$\alpha = 78.465 (5)^\circ$	$\mu = 0.26 \text{ mm}^{-1}$
$\beta = 82.546 (5)^\circ$	$T = 294 (2) \text{ K}$
$\gamma = 71.586 (4)^\circ$	Plate, colourless
$V = 674.3 (3) \text{ \AA}^3$	$0.26 \times 0.24 \times 0.20 \text{ mm}$

Data collection

Bruker SMART CCD area-detector diffractometer	2374 independent reflections
Radiation source: fine-focus sealed tube	1929 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{\text{int}} = 0.016$
$T = 294(2) \text{ K}$	$\theta_{\text{max}} = 25.0^\circ$
φ and ω scans	$\theta_{\text{min}} = 2.0^\circ$
Absorption correction: multi-scan (SADABS; Bruker, 1997)	$h = -9 \rightarrow 6$
$T_{\text{min}} = 0.936$, $T_{\text{max}} = 0.951$	$k = -10 \rightarrow 9$
3506 measured reflections	$l = -11 \rightarrow 12$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.040$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.108$	$w = 1/[\sigma^2(F_o^2) + (0.045P)^2 + 0.4673P]$
$S = 1.06$	where $P = (F_o^2 + 2F_c^2)/3$
2374 reflections	$(\Delta/\sigma)_{\text{max}} < 0.001$
176 parameters	$\Delta\rho_{\text{max}} = 0.41 \text{ e \AA}^{-3}$
5 restraints	$\Delta\rho_{\text{min}} = -0.33 \text{ e \AA}^{-3}$
Primary atom site location: structure-invariant direct methods	Extinction correction: none

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 $F^2 > 2\sigma(F^2)$ 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)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
S1	0.14016 (7)	0.73866 (7)	0.24152 (5)	0.03302 (19)
O1	0.4452 (2)	0.7411 (3)	0.46414 (17)	0.0535 (5)
H1	0.547 (2)	0.720 (4)	0.457 (4)	0.080*
O2	0.3063 (3)	0.7840 (3)	0.24406 (19)	0.0642 (6)
H2	0.344 (5)	0.760 (5)	0.319 (2)	0.096*
O3	0.0141 (2)	0.8333 (2)	0.33050 (17)	0.0468 (5)
O4	0.1771 (3)	0.5626 (3)	0.2834 (2)	0.0752 (7)
O5	0.0982 (3)	0.7967 (3)	0.10455 (17)	0.0676 (6)
N1	0.1898 (2)	0.8477 (2)	0.83066 (18)	0.0273 (4)
H1A	0.164 (3)	0.832 (3)	0.9156 (11)	0.033*
H1B	0.124 (2)	0.9428 (18)	0.795 (2)	0.033*
C1	0.3968 (3)	0.7257 (3)	0.6054 (2)	0.0361 (5)
H1C	0.4668	0.6187	0.6519	0.043*
C2	0.4211 (3)	0.8696 (3)	0.6595 (2)	0.0349 (5)
H2A	0.3553	0.9749	0.6101	0.042*
H2B	0.5396	0.8656	0.6444	0.042*
C3	0.3682 (3)	0.8660 (3)	0.8082 (2)	0.0302 (5)
C4	0.1464 (3)	0.7153 (3)	0.7725 (2)	0.0325 (5)
C5	0.2122 (3)	0.7299 (3)	0.6255 (2)	0.0368 (5)
H5A	0.1989	0.6383	0.5891	0.044*
H5B	0.1442	0.8343	0.5763	0.044*
C6	0.4904 (3)	0.7243 (3)	0.8968 (2)	0.0427 (6)
H6A	0.4410	0.7137	0.9870	0.064*
H6B	0.5952	0.7495	0.8946	0.064*
H6C	0.5116	0.6208	0.8645	0.064*
C7	0.3528 (3)	1.0332 (3)	0.8499 (3)	0.0435 (6)
H7A	0.2729	1.1223	0.7972	0.065*
H7B	0.4614	1.0530	0.8359	0.065*
H7C	0.3145	1.0291	0.9427	0.065*
C8	-0.0472 (3)	0.7621 (3)	0.7869 (3)	0.0463 (6)
H8A	-0.0831	0.6808	0.7552	0.069*
H8B	-0.0942	0.8711	0.7354	0.069*
H8C	-0.0859	0.7639	0.8792	0.069*

supplementary materials

C9	0.2196 (4)	0.5397 (3)	0.8522 (3)	0.0497 (7)
H9A	0.1695	0.4635	0.8278	0.075*
H9B	0.1950	0.5431	0.9459	0.075*
H9C	0.3401	0.5023	0.8328	0.075*
O6	0.7835 (3)	0.6591 (3)	0.4742 (2)	0.0653 (6)
H6D	0.858 (4)	0.702 (5)	0.442 (4)	0.098*
H6E	0.814 (5)	0.591 (4)	0.540 (3)	0.098*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0324 (3)	0.0395 (3)	0.0236 (3)	-0.0090 (2)	0.0009 (2)	-0.0016 (2)
O1	0.0404 (10)	0.0952 (15)	0.0292 (9)	-0.0222 (11)	0.0056 (8)	-0.0224 (9)
O2	0.0442 (11)	0.1171 (19)	0.0365 (11)	-0.0394 (12)	0.0015 (8)	-0.0028 (11)
O3	0.0428 (10)	0.0516 (11)	0.0402 (10)	-0.0059 (8)	0.0048 (8)	-0.0131 (8)
O4	0.0928 (17)	0.0381 (11)	0.0867 (17)	-0.0123 (11)	-0.0044 (13)	-0.0057 (11)
O5	0.0535 (12)	0.1205 (19)	0.0234 (9)	-0.0260 (12)	-0.0040 (8)	0.0006 (10)
N1	0.0263 (10)	0.0300 (10)	0.0244 (9)	-0.0080 (8)	0.0000 (7)	-0.0038 (8)
C1	0.0352 (13)	0.0462 (14)	0.0251 (12)	-0.0095 (11)	0.0008 (9)	-0.0083 (10)
C2	0.0320 (12)	0.0450 (14)	0.0287 (12)	-0.0159 (10)	0.0019 (9)	-0.0040 (10)
C3	0.0272 (11)	0.0382 (12)	0.0264 (11)	-0.0122 (9)	-0.0018 (9)	-0.0043 (9)
C4	0.0349 (12)	0.0315 (12)	0.0345 (13)	-0.0155 (10)	-0.0001 (10)	-0.0055 (9)
C5	0.0376 (13)	0.0440 (14)	0.0328 (12)	-0.0144 (11)	-0.0019 (10)	-0.0123 (10)
C6	0.0321 (13)	0.0579 (16)	0.0334 (13)	-0.0081 (11)	-0.0067 (10)	-0.0030 (11)
C7	0.0448 (15)	0.0486 (15)	0.0456 (15)	-0.0221 (12)	-0.0031 (11)	-0.0139 (12)
C8	0.0398 (14)	0.0552 (16)	0.0521 (16)	-0.0243 (12)	0.0039 (12)	-0.0158 (13)
C9	0.0630 (18)	0.0324 (13)	0.0528 (16)	-0.0184 (12)	-0.0020 (13)	0.0003 (11)
O6	0.0456 (12)	0.0785 (16)	0.0653 (15)	-0.0238 (11)	0.0011 (10)	0.0083 (11)

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

S1—O4	1.419 (2)	C4—C8	1.529 (3)
S1—O5	1.4411 (18)	C4—C9	1.530 (3)
S1—O3	1.4476 (18)	C4—C5	1.530 (3)
S1—O2	1.555 (2)	C5—H5A	0.9700
O1—C1	1.443 (3)	C5—H5B	0.9700
O1—H1	0.81 (2)	C6—H6A	0.9600
O2—H2	0.83 (2)	C6—H6B	0.9600
N1—C3	1.528 (3)	C6—H6C	0.9600
N1—C4	1.529 (3)	C7—H7A	0.9600
N1—H1A	0.86 (2)	C7—H7B	0.9600
N1—H1B	0.86 (2)	C7—H7C	0.9600
C1—C5	1.515 (3)	C8—H8A	0.9600
C1—C2	1.519 (3)	C8—H8B	0.9600
C1—H1C	0.9800	C8—H8C	0.9600
C2—C3	1.528 (3)	C9—H9A	0.9600
C2—H2A	0.9700	C9—H9B	0.9600
C2—H2B	0.9700	C9—H9C	0.9600
C3—C7	1.529 (3)	O6—H6D	0.82 (2)

C3—C6	1.531 (3)	O6—H6E	0.81 (2)
O4—S1—O5	114.56 (15)	N1—C4—C5	107.47 (17)
O4—S1—O3	112.68 (13)	C8—C4—C5	111.10 (19)
O5—S1—O3	111.13 (12)	C9—C4—C5	112.8 (2)
O4—S1—O2	107.34 (14)	C1—C5—C4	112.66 (18)
O5—S1—O2	103.30 (11)	C1—C5—H5A	109.1
O3—S1—O2	107.04 (12)	C4—C5—H5A	109.1
C1—O1—H1	106 (3)	C1—C5—H5B	109.1
S1—O2—H2	114 (3)	C4—C5—H5B	109.1
C3—N1—C4	120.80 (17)	H5A—C5—H5B	107.8
C3—N1—H1A	107.9 (16)	C3—C6—H6A	109.5
C4—N1—H1A	107.7 (16)	C3—C6—H6B	109.5
C3—N1—H1B	105.5 (16)	H6A—C6—H6B	109.5
C4—N1—H1B	105.6 (16)	C3—C6—H6C	109.5
H1A—N1—H1B	109 (2)	H6A—C6—H6C	109.5
O1—C1—C5	108.04 (18)	H6B—C6—H6C	109.5
O1—C1—C2	109.83 (19)	C3—C7—H7A	109.5
C5—C1—C2	110.27 (19)	C3—C7—H7B	109.5
O1—C1—H1C	109.6	H7A—C7—H7B	109.5
C5—C1—H1C	109.6	C3—C7—H7C	109.5
C2—C1—H1C	109.6	H7A—C7—H7C	109.5
C1—C2—C3	113.44 (18)	H7B—C7—H7C	109.5
C1—C2—H2A	108.9	C4—C8—H8A	109.5
C3—C2—H2A	108.9	C4—C8—H8B	109.5
C1—C2—H2B	108.9	H8A—C8—H8B	109.5
C3—C2—H2B	108.9	C4—C8—H8C	109.5
H2A—C2—H2B	107.7	H8A—C8—H8C	109.5
N1—C3—C2	107.19 (16)	H8B—C8—H8C	109.5
N1—C3—C7	105.65 (18)	C4—C9—H9A	109.5
C2—C3—C7	111.28 (19)	C4—C9—H9B	109.5
N1—C3—C6	110.75 (18)	H9A—C9—H9B	109.5
C2—C3—C6	112.80 (19)	C4—C9—H9C	109.5
C7—C3—C6	108.92 (19)	H9A—C9—H9C	109.5
N1—C4—C8	105.19 (18)	H9B—C9—H9C	109.5
N1—C4—C9	111.11 (19)	H6D—O6—H6E	111 (4)
C8—C4—C9	108.9 (2)		
O1—C1—C2—C3	178.44 (18)	C3—N1—C4—C8	-167.05 (19)
C5—C1—C2—C3	59.5 (2)	C3—N1—C4—C9	75.2 (2)
C4—N1—C3—C2	47.9 (2)	C3—N1—C4—C5	-48.6 (2)
C4—N1—C3—C7	166.70 (19)	O1—C1—C5—C4	-179.71 (19)
C4—N1—C3—C6	-75.5 (2)	C2—C1—C5—C4	-59.7 (3)
C1—C2—C3—N1	-50.8 (2)	N1—C4—C5—C1	51.7 (3)
C1—C2—C3—C7	-165.8 (2)	C8—C4—C5—C1	166.3 (2)
C1—C2—C3—C6	71.4 (2)	C9—C4—C5—C1	-71.1 (3)

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>
O2—H2 \cdots O1	0.83 (2)	1.76 (2)	2.576 (3)	168 (4)

supplementary materials

N1—H1A···O5 ⁱ	0.86 (2)	1.933 (17)	2.795 (3)	178 (2)
N1—H1B···O3 ⁱⁱ	0.86 (2)	2.154 (19)	3.002 (3)	168 (2)
O6—H6D···O3 ⁱⁱⁱ	0.82 (2)	2.06 (2)	2.874 (3)	169 (4)
O6—H6E···O4 ^{iv}	0.81 (2)	2.00 (2)	2.790 (3)	165 (4)

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

Fig. 1

