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

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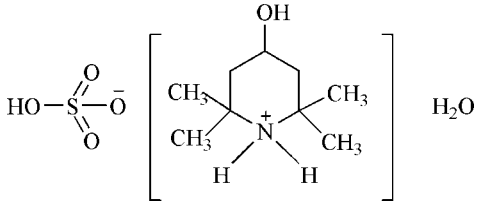
Key indicators: single-crystal X-ray study; $T$ = 294 K; mean $\sigma$(C–C) = 0.004 Å; $R$ factor = 0.040; $wR$ factor = 0.108; data-to-parameter ratio = 13.5.

In the title compound, $C_9H_{20}NO^+\cdot HO_4S^-\cdot H_2O$, the piperidinium ring adopts a chair conformation. Intermolecular O—H···O and N—H···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

$C_9H_{20}NO^+\cdot HO_4S^-\cdot H_2O$
$M_r$ = 273.34
Triclinic, $P\overline{1}$
$a$ = 8.334 (3) Å
$b$ = 8.518 (3) Å
$c$ = 10.245 (3) Å
$\alpha$ = 78.465 (5)°
$\beta$ = 82.546 (5)°
$\gamma$ = 71.586 (4)°
$V$ = 674.3 (3) Å$^3$
$Z$ = 2
Mo $K\alpha$ radiation
$\mu$ = 0.26 mm$^{-1}$
$T$ = 294 (2) K
0.26 × 0.24 × 0.20 mm

### Data collection

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

### 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
$\Delta\rho_{max}$ = 0.41 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.33 e Å$^{-3}$

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| O2—H2···O1 | 0.83 (2) | 1.76 (2) | 2.576 (3) | 168 (4) |
| N1—H1$A$···O5$^{i}$ | 0.86 (2) | 1.933 (17) | 2.795 (3) | 178 (2) |
| N1—H1$B$···O3$^{ii}$ | 0.86 (2) | 2.154 (19) | 3.002 (3) | 168 (2) |
| O6—H6$D$···O3$^{iii}$ | 0.82 (2) | 2.06 (2) | 2.874 (3) | 169 (4) |
| O6—H6$E$···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.

# supporting information

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

**Li Xiao, Yun-Hui Zhang, Ying Cui, Xing-Hua Jin and Wei Wang**

### S1. 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···O and N—H···O hydrogen bonds (Table 1) form an extensive three-dimensional network, which consolidates the packing.

### S2. Experimental

2,2,6,6-Tetramethylpiperidin-4-ol (40.0 g, 254 mmol) was dissolved in 98% $H_2SO_4$ (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.

### S3. 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 wrere refined as riding, with $U_{iso}$(H)=1.2–1.5$U_{eq}$ of the parent atom.

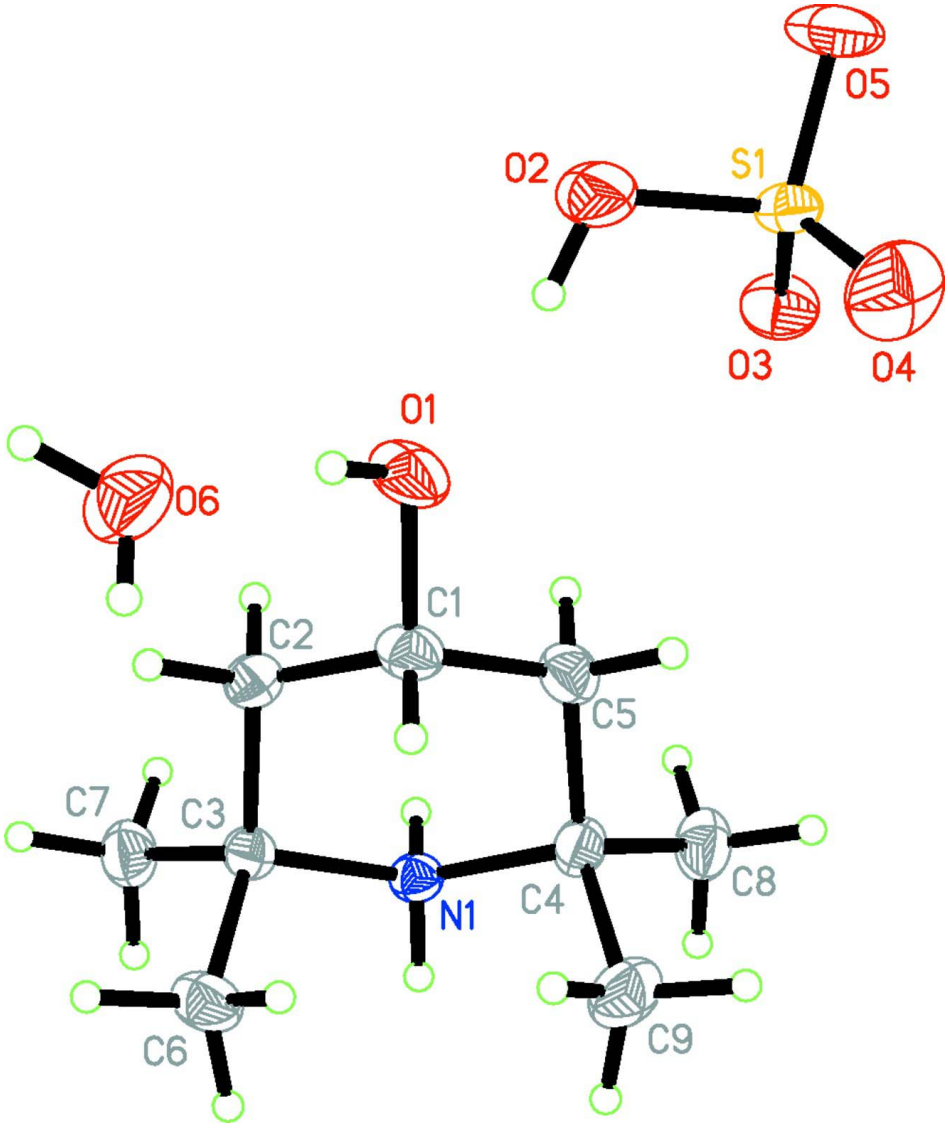


**Figure 1**

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*

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

*Data collection*

Bruker SMART CCD area-detector diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
$\varphi$ and $\omega$ scans
Absorption correction: multi-scan (*SADABS*; Bruker, 1997)
$T_{min}$ = 0.936, $T_{max}$ = 0.951
3506 measured reflections
2374 independent reflections
1929 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.016
$\theta_{max}$ = 25.0°, $\theta_{min}$ = 2.0°
$h = -9 \rightarrow 6$
$k = -10 \rightarrow 9$
$l = -11 \rightarrow 12$

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.040
$wR(F^2)$ = 0.108
$S$ = 1.06
2374 reflections
176 parameters
5 restraints
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
$w = 1/[\sigma^2(F_o^2) + (0.045P)^2 + 0.4673P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.41 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.33 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 (Å²)*

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| 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* |
| 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 (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| 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 (Å, º)*

| | | | |
|---|---|---|---|
| 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 (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| O2—H2···O1 | 0.83 (2) | 1.76 (2) | 2.576 (3) | 168 (4) |
| N1—H1*A*···O5$^{i}$ | 0.86 (2) | 1.93 (2) | 2.795 (3) | 178 (2) |
| N1—H1*B*···O3$^{ii}$ | 0.86 (2) | 2.15 (2) | 3.002 (3) | 168 (2) |
| O6—H6*D*···O3$^{iii}$ | 0.82 (2) | 2.06 (2) | 2.874 (3) | 169 (4) |
| O6—H6*E*···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.