# organic compounds

# 4,4,5,5-Tetramethyl-2-(4-pyridinio)-2-imidazoline-1-oxyl-3-oxide perchlorate

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The crystal structure of the title compound, $C_{12}H_{17}N_3O_2^{+}\cdot ClO_4^{-}$, consists of 4,4,5,5-tetramethyl-2-(4-pyridinio)imidazoline-1-oxyl-3-oxide radical cations and perchlorate anions. Both the cation and the Cl atom of the anion are located on the same twofold rotation axis, and the crystal structure shows the average structure for the radical cation. The five-membered ring assumes a half-chair conformation. The cation links with the anion via N—H···O hydrogen bonding.

## Related literature

For general background, see: Wang *et al.* (2004); Li *et al.* (2003); Kahn *et al.* (2000); Tsukahara *et al.* (2003); Fettouhi *et al.* (2003); Zhang *et al.* (2004); Fokin *et al.* (2004); Chang *et al.* (2009). For the synthesis, see: Ullman *et al.* (1970, 1972).
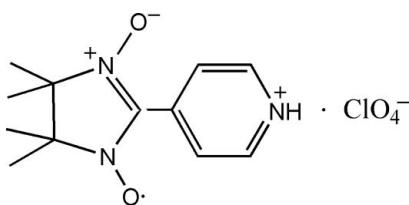


## Experimental

### Crystal data

| | |
|---|---|
| $C_{12}H_{17}N_3O_2^{+}\cdot ClO_4^{-}$ | $V = 3092.6$ (10) Å$^3$ |
| $M_r = 334.74$ | $Z = 8$ |
| Orthorhombic, $Fdd2$ | Mo $K\alpha$ radiation |
| $a = 17.485$ (4) Å | $\mu = 0.28$ mm$^{-1}$ |
| $b = 11.854$ (2) Å | $T = 273$ K |
| $c = 14.921$ (2) Å | $0.33 \times 0.26 \times 0.23$ mm |

### Data collection

| | |
|---|---|
| Bruker SMART CCD area-detector diffractometer | 3994 measured reflections |
| Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996) | 1204 independent reflections |
| | 1169 reflections with $I > 2\sigma(I)$ |
| $T_{min} = 0.915$, $T_{max} = 0.930$ | $R_{int} = 0.016$ |

### Refinement

| | |
|---|---|
| $R[F^2 > 2\sigma(F^2)] = 0.033$ | H-atom parameters constrained |
| $wR(F^2) = 0.102$ | $\Delta\rho_{max} = 0.27$ e Å$^{-3}$ |
| $S = 1.06$ | $\Delta\rho_{min} = -0.15$ e Å$^{-3}$ |
| 1204 reflections | Absolute structure: Flack (1983), 457 Friedel pairs |
| 103 parameters | Flack parameter: 0.12 (10) |
| 1 restraint | |

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| N1—H1$B$···O3 | 0.86 | 2.20 | 2.963 (4) | 149 |

Data collection: *SMART* (Bruker, 2002); cell refinement: *SAINT* (Bruker, 2002); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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# supporting information

## 4,4,5,5-Tetramethyl-2-(4-pyridinio)-2-imidazoline-1-oxyl-3-oxide perchlorate

### Zhi-Yong Gao, Jiu-Li Chang, Dong Xian and Kai Jiang

### S1. Comment

The major research aims in the field of molecular magnetism are on one hand the chemical design of molecular assemblies that exhibit a spontaneous magnetization and on the other hand the rationalization of magneto-structural correlation (Wang *et al.*, 2004; Li *et al.*, 2003; Kahn *et al.*, 2000; Tsukahara *et al.*, 2003). Nitronyl nitroxide radicals (NITR), stable organic radicals, have played an important role in the design and synthesis of molecular magnetic materials (Fettouhi *et al.*, 2003; Zhang *et al.*, 2004; Fokin *et al.*, 2004). Many structures have been investigated on the coordination of nitronyl nitroxide radicals to metals, but less on the non-covalent weak interactions of nitronyl nitroxide radicals with other molecules (Chang *et al.*, 2009). Taking account of these, we report on the molecular assemblies of NITpPy and perchlorate anion in order to further understand the coordination chemistry of nitronyl nitroxide radicals.

The structure of the title compound is shown in Fig. 1. The compound consists of a discrete [NITpPyH] cation and a perchlorate anion. NITpPy acts as a proton sponge by accepting a proton. The transfer of protons results in symmetric intermolecular hydrogen bonds: the double hydrogen bonds occur between two oxygen atoms from perchlorate anion and one nitrogen atom from the pyridyl ring (Table 1). The nitronyl nitroxide fragment O—N—C—N—O is almost coplanar, but make a dihedral angle of 17.0° with the pyridyl ring. In the unit cell cations and anions are alternatively arranged.

### S2. Experimental

NITpPy was synthesized according to a literature procedure (Ullman *et al.*, 1970; Ullman *et al.*, 1972). The title compound was obtained serendipitously from the reaction of copper perchlorate hydrate (1 mmol) and NITpPy (2 mmol) in methanol (10 ml). The mixture was stirred for 4 h at room temperature and then filtered. Subsequently, the filtrate was diffused with diethyl ether vapor and dark-purple block crystals were obtained one week later.

### S3. Refinement

The H atoms were positioned geometrically and refined using the riding-model approximation, with C—H = 0.93 (aromatic), 0.96 Å (methyl) and N—H = 0.86 Å, and $U_{iso}(H) = 1.5U_{eq}(C)$ for methyl groups and $1.2U_{eq}(C,N)$ for others.
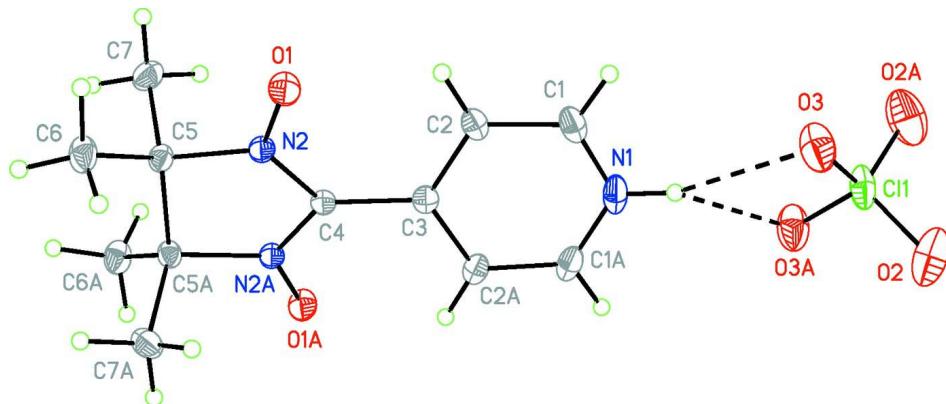
**Figure 1**

The molecular structure of the title compound with atom labeling. The thermal ellipsoids are drawn at 30% probability level [symmetry code: (A) -x,-y+1,z]. Dashed lines indicate hydrogen bonding.

## 4,4,5,5-Tetramethyl-2-(4-pyridinio)-2-imidazoline-1-oxyl-3-oxide perchlorate

*Crystal data*
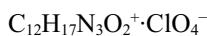
| | |
|---|---|
| $C_{12}H_{17}N_3O_2{}^+ \cdot ClO_4{}^-$ | $F(000) = 1400$ |
| $M_r = 334.74$ | $D_x = 1.438$ Mg m$^{-3}$ |
| Orthorhombic, $Fdd2$ | Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å |
| Hall symbol: F 2 -2d | Cell parameters from 2949 reflections |
| $a = 17.485$ (4) Å | $\theta = 2.3$–$29.0°$ |
| $b = 11.854$ (2) Å | $\mu = 0.28$ mm$^{-1}$ |
| $c = 14.921$ (2) Å | $T = 273$ K |
| $V = 3092.6$ (10) Å$^3$ | Block, dark-purple |
| $Z = 8$ | $0.33 \times 0.26 \times 0.23$ mm |

*Data collection*

| | |
|---|---|
| Bruker SMART CCD area-detector diffractometer | 3994 measured reflections |
| Radiation source: fine-focus sealed tube | 1204 independent reflections |
| Graphite monochromator | 1169 reflections with $I > 2\sigma(I)$ |
| $\varphi$ and $\omega$ scans | $R_{int} = 0.016$ |
| Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996) | $\theta_{max} = 25.5°$, $\theta_{min} = 2.5°$ |
| | $h = -21 \rightarrow 20$ |
| $T_{min} = 0.915$, $T_{max} = 0.930$ | $k = -11 \rightarrow 14$ |
| | $l = -15 \rightarrow 18$ |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | Hydrogen site location: inferred from neighbouring sites |
| Least-squares matrix: full | H-atom parameters constrained |
| $R[F^2 > 2\sigma(F^2)] = 0.033$ | $w = 1/[\sigma^2(F_o^2) + (0.0762P)^2 + 1.0334P]$ |
| $wR(F^2) = 0.102$ | where $P = (F_o^2 + 2F_c^2)/3$ |
| $S = 1.06$ | $(\Delta/\sigma)_{max} < 0.001$ |
| 1204 reflections | $\Delta\rho_{max} = 0.27$ e Å$^{-3}$ |
| 103 parameters | $\Delta\rho_{min} = -0.15$ e Å$^{-3}$ |
| 1 restraint | Extinction correction: *SHELXTL* (Bruker, 2000), Fc$^*$=kFc[1+0.001xFc$^2\lambda^3$/sin(2$\theta$)]$^{-1/4}$ |
| Primary atom site location: structure-invariant direct methods | Extinction coefficient: 0.0026 (5) |
| Secondary atom site location: difference Fourier map | |

| Absolute structure: Flack (1983), 457 Friedel pairs | Absolute structure parameter: 0.12 (10) |
|---|---|

*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 ($Å^2$)*

|  | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| Cl1 | 0.0000 | 0.5000 | 0.05797 (7) | 0.0787 (4) |
| O2 | 0.0203 (2) | 0.4065 (5) | 0.0039 (3) | 0.1497 (15) |
| O3 | 0.06280 (15) | 0.5281 (3) | 0.1140 (2) | 0.1055 (9) |
| N1 | 0.0000 | 0.5000 | 0.2971 (2) | 0.0684 (10) |
| H1B | 0.0000 | 0.5000 | 0.2395 | 0.082* |
| N2 | 0.05399 (9) | 0.54721 (12) | 0.62987 (12) | 0.0399 (4) |
| C1 | 0.04640 (17) | 0.5698 (2) | 0.33929 (18) | 0.0626 (6) |
| H1A | 0.0785 | 0.6169 | 0.3067 | 0.075* |
| C2 | 0.04743 (13) | 0.57302 (19) | 0.43134 (16) | 0.0520 (5) |
| H2A | 0.0793 | 0.6232 | 0.4614 | 0.062* |
| C3 | 0.0000 | 0.5000 | 0.4789 (2) | 0.0417 (6) |
| C4 | 0.0000 | 0.5000 | 0.5764 (2) | 0.0379 (6) |
| C5 | 0.02991 (11) | 0.54883 (16) | 0.72622 (14) | 0.0425 (5) |
| C6 | 0.09853 (14) | 0.5301 (2) | 0.78664 (19) | 0.0630 (6) |
| H6A | 0.1322 | 0.5939 | 0.7827 | 0.095* |
| H6B | 0.1253 | 0.4634 | 0.7680 | 0.095* |
| H6C | 0.0816 | 0.5213 | 0.8474 | 0.095* |
| C7 | −0.00457 (14) | 0.66478 (19) | 0.74312 (19) | 0.0616 (7) |
| H7A | 0.0352 | 0.7206 | 0.7422 | 0.092* |
| H7B | −0.0293 | 0.6654 | 0.8006 | 0.092* |
| H7C | −0.0414 | 0.6815 | 0.6972 | 0.092* |
| O1 | 0.11652 (8) | 0.59302 (15) | 0.60418 (12) | 0.0599 (5) |

*Atomic displacement parameters ($Å^2$)*

|  | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Cl1 | 0.0631 (5) | 0.1338 (9) | 0.0392 (5) | −0.0116 (5) | 0.000 | 0.000 |
| O2 | 0.154 (3) | 0.199 (4) | 0.096 (3) | 0.023 (3) | 0.013 (2) | −0.053 (3) |
| O3 | 0.0789 (14) | 0.167 (2) | 0.0707 (17) | −0.0372 (15) | −0.0088 (13) | 0.0105 (16) |
| N1 | 0.092 (2) | 0.0776 (18) | 0.0360 (17) | 0.0404 (17) | 0.000 | 0.000 |
| N2 | 0.0356 (7) | 0.0440 (7) | 0.0400 (10) | −0.0075 (6) | −0.0005 (7) | −0.0002 (6) |
| C1 | 0.0729 (15) | 0.0692 (14) | 0.0457 (14) | 0.0203 (11) | 0.0104 (11) | 0.0154 (11) |
| C2 | 0.0547 (12) | 0.0570 (10) | 0.0443 (13) | 0.0068 (9) | 0.0035 (9) | 0.0088 (9) |

| | | | | | |
|---|---|---|---|---|---|
| C3 | 0.0394 (13) | 0.0430 (12) | 0.0425 (18) | 0.0116 (10) | 0.000 | 0.000 |
| C4 | 0.0367 (12) | 0.0376 (12) | 0.0394 (18) | −0.0002 (9) | 0.000 | 0.000 |
| C5 | 0.0409 (10) | 0.0499 (10) | 0.0368 (11) | −0.0056 (9) | −0.0015 (9) | −0.0025 (8) |
| C6 | 0.0548 (12) | 0.0865 (15) | 0.0478 (15) | −0.0160 (12) | −0.0141 (11) | 0.0046 (11) |
| C7 | 0.0683 (14) | 0.0550 (11) | 0.0614 (17) | −0.0014 (10) | 0.0048 (12) | −0.0153 (10) |
| O1 | 0.0461 (7) | 0.0784 (10) | 0.0553 (11) | −0.0250 (7) | 0.0047 (7) | 0.0008 (8) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| Cl1—O2$^i$ | 1.416 (4) | C2—H2A | 0.9300 |
| Cl1—O2 | 1.416 (4) | C3—C2$^i$ | 1.393 (3) |
| Cl1—O3 | 1.420 (3) | C3—C4 | 1.455 (4) |
| Cl1—O3$^i$ | 1.420 (3) | C4—N2$^i$ | 1.357 (2) |
| N1—C1 | 1.318 (4) | C5—C6 | 1.517 (3) |
| N1—C1$^i$ | 1.318 (4) | C5—C7 | 1.522 (3) |
| N1—H1B | 0.8600 | C5—C5$^i$ | 1.560 (4) |
| N2—O1 | 1.280 (2) | C6—H6A | 0.9600 |
| N2—C4 | 1.357 (2) | C6—H6B | 0.9600 |
| N2—C5 | 1.498 (3) | C6—H6C | 0.9600 |
| C1—C2 | 1.374 (4) | C7—H7A | 0.9600 |
| C1—H1A | 0.9300 | C7—H7B | 0.9600 |
| C2—C3 | 1.393 (3) | C7—H7C | 0.9600 |
| | | | |
| O2$^i$—Cl1—O2 | 110.5 (5) | N2—C4—N2$^i$ | 108.0 (3) |
| O2$^i$—Cl1—O3 | 110.2 (3) | N2—C4—C3 | 126.01 (13) |
| O2—Cl1—O3 | 109.0 (2) | N2$^i$—C4—C3 | 126.01 (13) |
| O2$^i$—Cl1—O3$^i$ | 109.0 (2) | N2—C5—C6 | 110.26 (18) |
| O2—Cl1—O3$^i$ | 110.2 (3) | N2—C5—C7 | 106.37 (18) |
| O3—Cl1—O3$^i$ | 107.9 (2) | C6—C5—C7 | 110.28 (19) |
| C1—N1—C1$^i$ | 123.0 (3) | N2—C5—C5$^i$ | 100.31 (10) |
| C1—N1—H1B | 118.5 | C6—C5—C5$^i$ | 114.96 (17) |
| C1$^i$—N1—H1B | 118.5 | C7—C5—C5$^i$ | 113.9 (2) |
| O1—N2—C4 | 126.40 (18) | C5—C6—H6A | 109.5 |
| O1—N2—C5 | 121.47 (16) | C5—C6—H6B | 109.5 |
| C4—N2—C5 | 111.96 (16) | H6A—C6—H6B | 109.5 |
| N1—C1—C2 | 120.2 (3) | C5—C6—H6C | 109.5 |
| N1—C1—H1A | 119.9 | H6A—C6—H6C | 109.5 |
| C2—C1—H1A | 119.9 | H6B—C6—H6C | 109.5 |
| C1—C2—C3 | 118.9 (2) | C5—C7—H7A | 109.5 |
| C1—C2—H2A | 120.5 | C5—C7—H7B | 109.5 |
| C3—C2—H2A | 120.5 | H7A—C7—H7B | 109.5 |
| C2$^i$—C3—C2 | 118.8 (3) | C5—C7—H7C | 109.5 |
| C2$^i$—C3—C4 | 120.61 (16) | H7A—C7—H7C | 109.5 |
| C2—C3—C4 | 120.61 (16) | H7B—C7—H7C | 109.5 |
| | | | |
| C1$^i$—N1—C1—C2 | −0.68 (16) | C2—C3—C4—N2 | −15.56 (13) |
| N1—C1—C2—C3 | 1.3 (3) | C2$^i$—C3—C4—N2$^i$ | −15.56 (13) |
| C1—C2—C3—C2$^i$ | −0.65 (15) | C2—C3—C4—N2$^i$ | 164.44 (13) |

| | | | |
|---|---|---|---|
| C1—C2—C3—C4 | 179.35 (15) | O1—N2—C5—C6 | −39.6 (2) |
| O1—N2—C4—N2ⁱ | 175.0 (2) | C4—N2—C5—C6 | 144.69 (16) |
| C5—N2—C4—N2ⁱ | −9.58 (9) | O1—N2—C5—C7 | 80.0 (2) |
| O1—N2—C4—C3 | −5.0 (2) | C4—N2—C5—C7 | −95.74 (16) |
| C5—N2—C4—C3 | 170.42 (9) | O1—N2—C5—C5ⁱ | −161.21 (18) |
| C2ⁱ—C3—C4—N2 | 164.44 (13) | C4—N2—C5—C5ⁱ | 23.1 (2) |

Symmetry code: (i) −*x*, −*y*+1, *z*.

*Hydrogen-bond geometry (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N1—H1*B*···O3 | 0.86 | 2.20 | 2.963 (4) | 149 |