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2,2':6',2''-Terpyridine 1,1''-dioxide dihydrate

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Key indicators

Single-crystal X-ray study
 $T = 298$ K
Mean $\sigma(\text{C}-\text{C}) = 0.004$ Å
 R factor = 0.052
 wR factor = 0.156
Data-to-parameter ratio = 9.7For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The title compound, $\text{C}_{15}\text{H}_{11}\text{N}_3\text{O}_3 \cdot 2\text{H}_2\text{O}$, crystallizes with terpyridine dioxide molecules positioned on mirror planes in the space group $Pnma$. Catemeric assemblages of terpyridine molecules [$\text{C}-\text{H} \cdots \text{O}-\text{N}^+ = 3.386$ (4) Å] are linked by bridging water molecules [$\text{C}-\text{H} \cdots \text{O} = 3.288$ (4) and 3.386 (4) Å; $\text{O}-\text{H} \cdots \text{O}-\text{N}^+ = 2.837$ (3) and 2.878 (4) Å], giving stacks of two-dimensional undulating motifs.

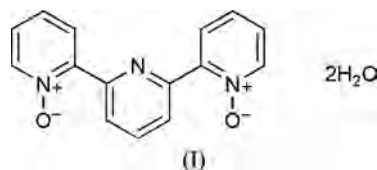
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Comment

Our recent report of the structure of terpyridine trioxide described the contribution of weak $\text{C}-\text{H} \cdots$ acceptor interactions to molecular organization (McKay *et al.*, 2004). Inspection of the structure revealed that each terpyridine trioxide molecule participates in ten $\text{C}-\text{H} \cdots \text{O}-\text{N}^+$ contacts with neighboring molecules, creating a three-dimensional network of hydrogen bonds. As a means to further explore the crystal chemistry of the terpyridine chemical framework, we recently prepared and crystallographically determined the structure of terpyridine dioxide dihydrate, (I).



The asymmetric unit of (I) contains one half-molecule of terpyridine dioxide and a water molecule (Fig. 1). Each terpyridine dioxide molecule is positioned on a mirror plane,

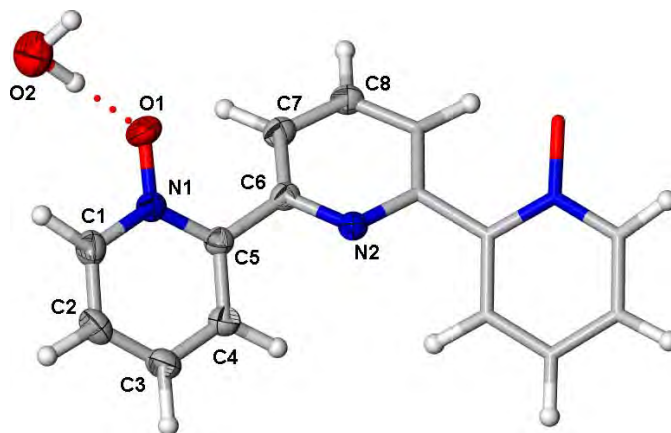


Figure 1

The molecular structure and labeling scheme of (I). Unlabeled atoms are related by the symmetry code $(x, -y + \frac{1}{2}, z)$. Displacement ellipsoids for the asymmetric unit are shown at the 50% probability level. The symmetry-related water molecule has been omitted.

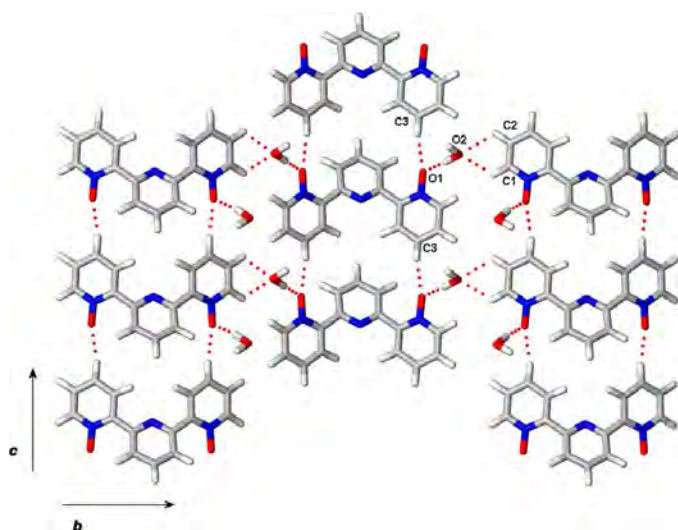


Figure 2
View of the molecular packing of (I), projected down the *a* axis, showing the hydrogen-bond network. Hydrogen bonds are shown as dotted lines.

passing through N2 and C8, with a pyridine–pyridine torsion angle N1–C5–C6–N2 of 147.0 (3)°. This conformation is less skewed than that in the trioxide adduct [−76.8 (2)°], presumably due to a more sterically favorable environment of the central pyridine fragment. Other notable geometric parameters for (I) are given in Table 1.

The supramolecular motifs observed in the structure of (I) are influenced by the construction of both strong and weak non-bonded contacts (Table 2). The *N*-oxide group of (I) provides a versatile acceptor that affects the packing preferences of the components. Inspection of Fig. 2 reveals C3–H...O1–⁺N1 contacts that link neighboring terpyridine molecules. These interactions propagate along the *c* axis to form chains consisting of translationally related molecules. Each water molecule participates in the crystal packing by forming two O2–H...O1–⁺N1 contacts that link adjacent terpyridine *N*-oxide groups. One such interaction bridges the one-dimensional terpyridine motifs to give an undulating molecular sheet (parallel to the *bc* plane). The second O2–H...O1–⁺N1 contact contributes to crystal stabilization by linking adjacent molecular sheets.

Experimental

Compound (I) was prepared using a modification of the procedure for direct oxidation of pyridine and pyrazine moieties (McKay *et al.*, 2001). Dimethyldioxirane (17.71 ml, 0.08 *M*) in acetone was stirred with terpyridine (150.4 mg, 0.6447 mol, Aldrich 98%) in acetone (2 ml, Fisher reagent grade) for 5 d at 300 K. Filtration of the mixture provided terpyridine dioxide as a colorless solid [92.2%, 157.6 mg; m.p. 502–507 K, *cf* 505–506 K (Thummel & Jahng, 1985)]. Crystals of (I) were obtained by diffusion of diethyl ether solution in dichloromethane at room temperature. Exhaustive measures were not undertaken to exclude water from the hygroscopic dimethyldioxirane/acetone reaction process and this provides a plausible entry point for the hydration of terpyridine dioxide. The oxidizing agent, dimethyldioxirane, was prepared (Murray & Jeyaraman, 1985) by

reacting potassium peroxomonosulfate (0.0390 mol) and NaHCO₃ (0.138 mol) in acetone (38.4 ml) and water (50 ml). Vigorous stirring of the mixture at 263 K followed by distillation (40–100 Torr) at ambient temperature resulted in 0.06–0.08 *M* dimethyldioxirane, as verified by titration against thioanisole.

Crystal data

C₁₅H₁₁N₃O₂·2H₂O
M_r = 301.30
 Orthorhombic, *Pnma*
a = 7.2590 (6) Å
b = 25.872 (3) Å
c = 7.4250 (15) Å
V = 1394.5 (3) Å³
Z = 4
D_x = 1.435 Mg m^{−3}

Mo *K*α radiation
 Cell parameters from 22 reflections
 θ = 23.5–26.8°
 μ = 0.11 mm^{−1}
T = 298 (2) K
 Plate, colorless
 0.42 × 0.36 × 0.10 mm

Data collection

Siemens P4 diffractometer
 $\theta/2\theta$ scans
 Absorption correction: none
 1830 measured reflections
 1302 independent reflections
 868 reflections with $I > 2\sigma(I)$
R_{int} = 0.024
 θ_{\max} = 25.4°

h = −8 → 1
k = −1 → 31
l = −1 → 8
 3 standard reflections
 every 97 reflections
 intensity decay: <3%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.052$
 $wR(F^2) = 0.156$
S = 1.06
 1302 reflections
 134 parameters

H atoms treated by a mixture of independent and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0881P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.18 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.23 \text{ e } \text{Å}^{-3}$

Table 1

Selected geometric parameters (Å, °).

O1–N1	1.318 (3)	C5–C6	1.476 (3)
N1–C5–C6	121.3 (2)	C4–C5–C6	120.9 (2)
N1–C5–C6–N2	147.0 (2)	C4–C5–C6–C7	144.0 (3)

Table 2

Hydrogen-bonding geometry (Å, °).

<i>D</i> –H... <i>A</i>	<i>D</i> –H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> –H... <i>A</i>
O2–H9...O1	1.01 (2)	1.83 (2)	2.837 (3)	174 (6)
O2–H10...O1 ⁱ	1.01 (2)	1.89 (3)	2.878 (4)	168 (7)
C1–H1...O2 ⁱⁱ	1.08	2.46	3.178 (4)	123
C2–H2...O2 ⁱⁱ	1.08	2.63	3.288 (4)	119
C3–H3...O1 ⁱⁱⁱ	1.08	2.34	3.386 (4)	162

Symmetry codes: (i) $\frac{1}{2} + x, y, \frac{1}{2} - z$; (ii) $2 - x, 1 - y, 1 - z$; (iii) $x, y, 1 + z$.

The OH and aryl H atoms were located in a difference density map and refined isotropically. The H-atom positions and *U*_{iso} values were refined and no constraints to the H atoms were applied during the refinement process [C–H = 0.87 (3)–0.91 (3) Å]. After refinement, the C–H bonds were adjusted to 1.08 Å for subsequent hydrogen-bond analysis (Fig. 2).

Data collection: *XSCANS* (Bruker, 1999); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *X-SEED* (Barbour, 2001); software used to prepare material for publication: *X-SEED*.

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