

2,2':6',2''-Terpyridine *N,N',N''*-trioxideScott E. McKay,^{a*}
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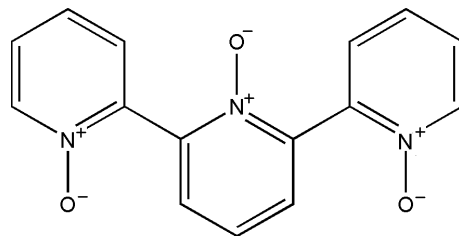
Key indicators

Single-crystal X-ray study
T = 213 K
Mean $\sigma(\text{C}-\text{C}) = 0.003 \text{ \AA}$
R factor = 0.033
wR factor = 0.082
Data-to-parameter ratio = 11.9For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The title compound, $\text{C}_{15}\text{H}_{11}\text{N}_3\text{O}_3$, crystallizes with molecules positioned on twofold rotation axes in space group $P4_32_12$. Five crystallographically unique intermolecular $\text{C}-\text{H}\cdots\text{O}-\text{N}^+$ contacts with $\text{H}\cdots\text{O} = 2.201(7)$, $2.50(2)$, $2.45(1)$, $2.38(1)$ and $2.35(2) \text{ \AA}$ produce a complex network of hydrogen bonds that assist in the stabilization of the crystal structure.

Comment

The significance of weak intermolecular interactions such as $\text{C}-\text{H}\cdots\text{O}$ hydrogen bonding is beginning to be reported for numerous compounds (Taylor & Kennard, 1982; Green, 1974; Desiraju, 1996; Steiner, 1997). These non-covalent interactions are estimated to be between 0.5 and $2.5 \text{ kcal mol}^{-1}$ (Blackstock *et al.*, 2001). Although the effect of classical hydrogen bonds (Pimentel & McClellan, 1960; Jeffrey, 1997) on solid-state structure has long been recognized, the importance of $\text{C}-\text{H}\cdots\text{O}$ contacts to molecular organization has only become apparent in the last decade (Desiraju, 1996; Steiner, 1997). Aryl H atoms, in particular, are known to participate in $\text{C}-\text{H}\cdots\text{O}$ hydrogen bonds because of the electronic influence of the corresponding sp^2 C_{aryl} atom.

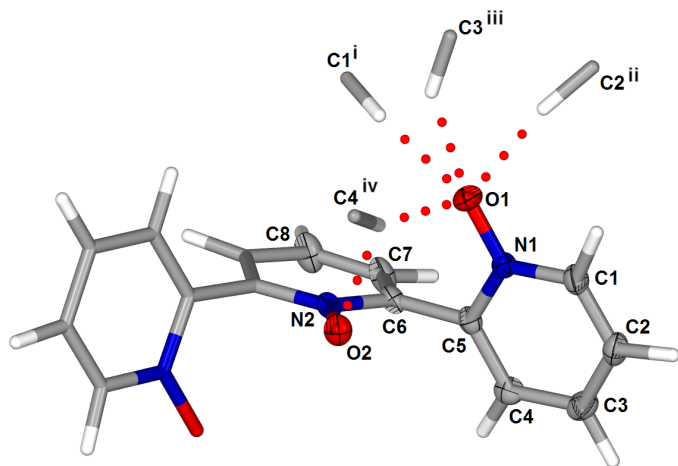


(I)

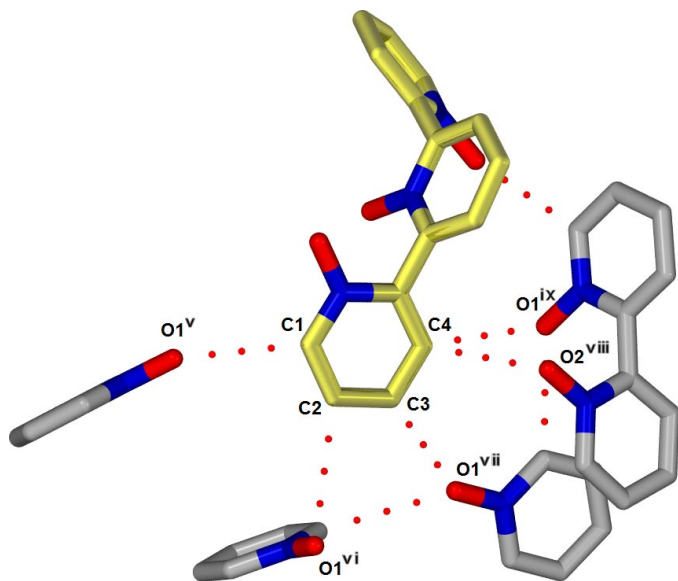
The title compound, (I), was prepared and its crystal structure analysed as a means to further understand the hydrogen-bond preferences of $\text{C}-\text{H}\cdots\text{O}-\text{N}^+$ interactions. Terpyridine compounds are well represented in the Cambridge Structural Database (CSD; Version 5.25; Allen, 2002), due in part to their excellent chelating and favorable hydrogen-bond-acceptor ability. By introducing three *N*-oxide functionalities to the terpyridine framework, this investigation provides an opportunity to explore the interdependency of three strong acceptors and molecular alignment.

Fig. 1 shows the structure of the asymmetric unit of (I), which contains a terpyridine trioxide molecule positioned on a twofold rotation axis. Molecules of (I) adopt a chiral conformation (space group $P4_32_12$) that results from the twist about each pyridine–pyridine bond [$\text{N1}-\text{C5}-\text{C6}-\text{N2} =$

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**Figure 1**

The molecular structure and labeling scheme of (I) (50% probability displacement ellipsoids for the asymmetric unit), showing the crystal environment near N-oxide atoms O1 and O2. [Symmetry codes: (i) $\frac{1}{2} + y, \frac{1}{2} - x, \frac{1}{4} + z$; (ii) $\frac{3}{2} - x, y - \frac{1}{2}, -z - \frac{1}{4}$; (iii) $y, x - 1, -z$; (iv) $x - \frac{1}{4}, \frac{1}{4} - y, \frac{1}{4} - z$.]

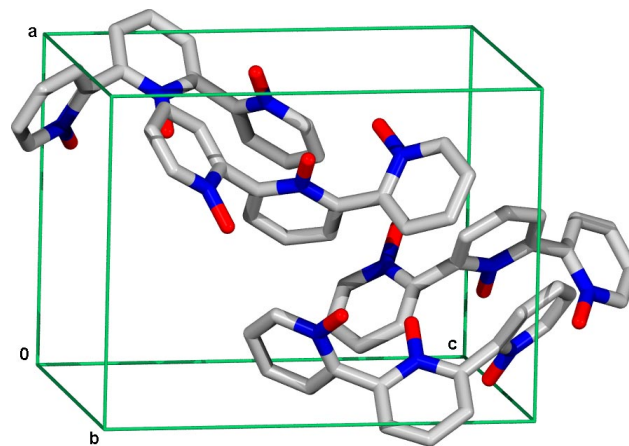
**Figure 2**

View of the C—H...O⁺N hydrogen-bond interactions for (I). H atoms have been omitted. [Symmetry codes: (v) $\frac{1}{2} - y, x - \frac{1}{2}, z - \frac{1}{2}$; (vi) $\frac{3}{2} - x, \frac{1}{2} + y, -z - \frac{1}{4}$; (vii) $1 - y, x, -z$; (viii) $\frac{3}{2} - y, x - \frac{1}{2}, z - \frac{1}{4}$; (ix) $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{4} - z$.]

$-76.8(2)^\circ$. Other selected geometric parameters are given in Table 1. Inspection of the close intermolecular contacts (Table 2, and Figs. 1 and 2) revealed that each molecule participates in ten (five unique) C—H...O⁺N interactions. Interestingly, this sizeable number of non-bonded contacts does not include the central pyridyl H atoms, presumably due to steric hindrance of the outer pyridyl rings on crystal-packing forces (Fig. 3).

Experimental

Oxygenation of commercially available terpyridine (440 mg, 1.72 mmol) with hydrogen peroxide (1.5 ml, 30%) in acetic acid

**Figure 3**

Crystal packing perspective of (I), showing the unit-cell contents. H atoms have been omitted.

provided the title terpyridine trioxide as a white high-melting and robust compound (Thummel & Jahng, 1985). Dissolving the terpyridine trioxide powder in boiling absolute ethanol, further concentration, and subsequent room-temperature acetone diffusion for 2 d afforded clear and colorless crystals. The terpyridine trioxide crystals were assessed using a polarizing microscope and a single crystal was attached to a nylon loop with paratone oil for the crystallographic investigation.

Crystal data

C₁₅H₁₁N₃O₃
M_r = 281.27
 Tetragonal, *P*4₃2₁2
a = 9.868 (1) Å
c = 12.801 (2) Å
V = 1246.6 (3) Å³
Z = 4
D_x = 1.499 Mg m⁻³

Mo *K*α radiation
 Cell parameters from 2341 reflections
 θ = 2.6–26.6°
 μ = 0.11 mm⁻¹
T = 213 (2) K
 Prisms, colorless
 0.20 × 0.20 × 0.10 mm

Data collection

Bruker *P4* CCD area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Bruker, 2000)
T_{min} = 0.961, *T_{max}* = 0.985
 9375 measured reflections

1420 independent reflections
 1296 reflections with *I* > 2σ(*I*)
R_{int} = 0.041
 θ_{max} = 27.4°
h = −12 → 12
k = −12 → 11
l = −16 → 15

Refinement

Refinement on *F*²
R [*F*² > 2σ(*F*²)] = 0.033
wR (*F*²) = 0.082
S = 1.07
 1420 reflections
 119 parameters
 All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0507P)^2 + 0.1514P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.18 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.24 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (Å, °).

O1—N1	1.3070 (19)	C5—C6	1.476 (2)
O2—N2	1.288 (3)		
N1—C5—C6	116.22 (16)	C4—C5—C6	123.53 (16)
N1—C5—C6—N2	−76.84 (18)	C4—C5—C6—C7	−74.9 (2)

Table 2
Hydrogen-bonding geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C1–H1 \cdots O1 ⁸	1.08	2.20	3.238 (2)	160
C2–H2 \cdots O1 ^{vi}	1.08	2.50	3.373 (2)	137
C3–H3 \cdots O1 ^{xi}	1.08	2.45	3.395 (2)	146
C4–H4 \cdots O1 ^{ix}	1.08	2.38	3.383 (2)	154
C4–H4 \cdots O2 ^{ix}	1.08	2.35	3.061 (2)	122

Symmetry codes: (vi) $\frac{3}{2}-x, \frac{1}{2}+y, -\frac{1}{4}-z$; (ix) $\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{4}-z$; (x) $\frac{1}{2}-y, x-\frac{1}{2}, z-\frac{1}{4}$; (xi) $1+y, x, -z$.

The aryl H atoms were located in a difference density map and refined isotropically. The C–H distances were then normalized to 1.08 Å for subsequent investigation of C–H \cdots O interactions (Fig. 2 and Table 2).

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2002); data reduction: *SAINT* and *XPREP* (Bruker, 2001); program(s) used to solve structure: *SHELXTL* (Bruker, 2000); program(s) used to refine structure: *SHELXTL*; molecular graphics: *XSEED* (Barbour, 2001); software used to prepare material for publication: *SHELXTL* and *XSEED*.

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