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# 2,2':6',2''-Terpyridine N,N',N''-trioxide

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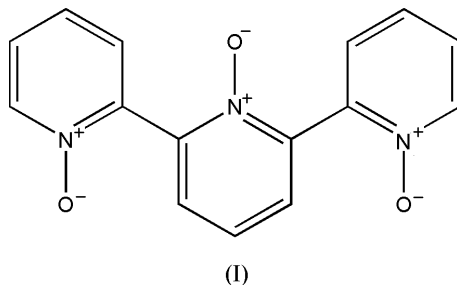
## Key indicators

Single-crystal X-ray study  
 $T = 213\text{ K}$   
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>.2,2':6',2''-Terpyridine  $N,N',N''$ -trioxide

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

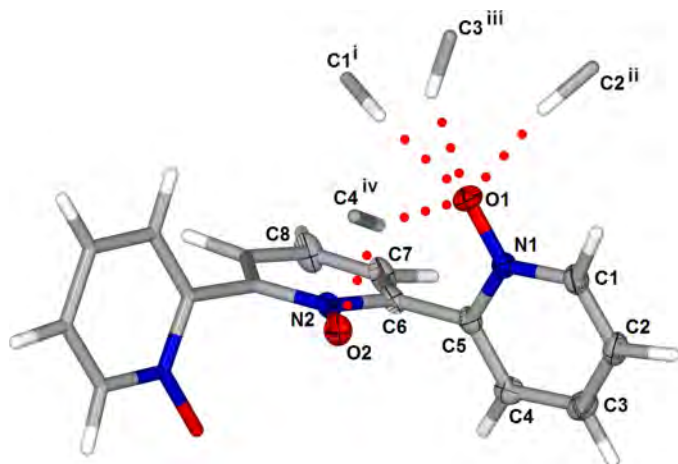
The significance of weak intermolecular interactions such as  $\text{C}-\text{H}\cdots\text{O}$  hydrogen bonding is beginning to be reported for numerous compounds (Taylor & Kennard, 1982; Green, 1974; Desiraju, 1996; Steiner, 1997). These non-covalent interactions are estimated to be between  $0.5$  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  $sp^2$   $\text{C}_{\text{aryl}}$  atom.



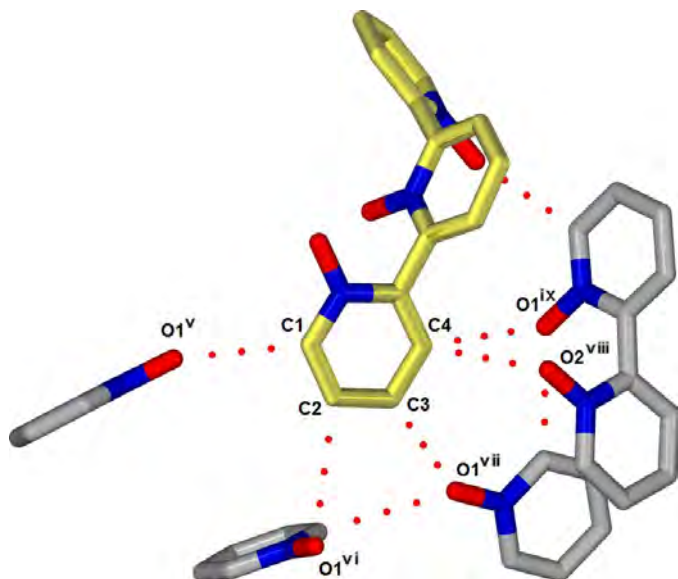
The title compound, (I), was prepared and its crystal structure analysed as a means to further understand the hydrogen-bond preferences of  $\text{C}-\text{H}\cdots\text{O}-\text{N}^+$  interactions. Terpyridine compounds are well represented in the Cambridge Structural Database (CSD; Version 5.25; Allen, 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)  $x - \frac{1}{4}, \frac{1}{4} - y, \frac{1}{4} - z$ .]

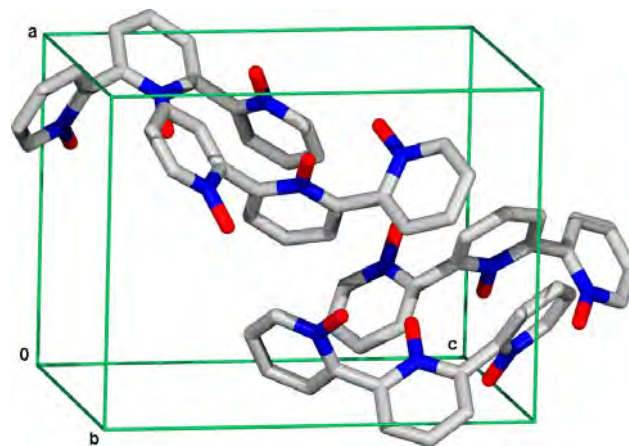
**Figure 2**

View of the C—H...O<sup>−</sup>+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<sup>−</sup>+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

C<sub>15</sub>H<sub>11</sub>N<sub>3</sub>O<sub>3</sub>  
*M<sub>r</sub>* = 281.27  
 Tetragonal, *P*4<sub>3</sub>2<sub>1</sub>2  
*a* = 9.868 (1) Å  
*c* = 12.801 (2) Å  
*V* = 1246.6 (3) Å<sup>3</sup>  
*Z* = 4  
*D<sub>x</sub>* = 1.499 Mg m<sup>−3</sup>

Mo *K*α radiation  
 Cell parameters from 2341 reflections  
 $\theta = 2.6\text{--}26.6^\circ$   
 $\mu = 0.11\text{ mm}^{-1}$   
*T* = 213 (2) K  
 Prisms, colorless  
 0.20 × 0.20 × 0.10 mm

### Data collection

Bruker *P4* CCD area-detector diffractometer  
 $\varphi$  and  $\omega$  scans  
 Absorption correction: multi-scan (SADABS; Bruker, 2000)  
*T<sub>min</sub>* = 0.961, *T<sub>max</sub>* = 0.985  
 9375 measured reflections

1420 independent reflections  
 1296 reflections with *I* > 2σ(*I*)  
*R<sub>int</sub>* = 0.041  
 $\theta_{\text{max}} = 27.4^\circ$   
*h* = −12 → 12  
*k* = −12 → 11  
*l* = −16 → 15

### Refinement

Refinement on *F*<sup>2</sup>  
*R*[*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.033  
*wR*(*F*<sup>2</sup>) = 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 <sup>8</sup>	1.08	2.20	3.238 (2)	160
C2—H2 $\cdots$ O1 <sup>vi</sup>	1.08	2.50	3.373 (2)	137
C3—H3 $\cdots$ O1 <sup>xi</sup>	1.08	2.45	3.395 (2)	146
C4—H4 $\cdots$ O1 <sup>ix</sup>	1.08	2.38	3.383 (2)	154
C4—H4 $\cdots$ O2 <sup>ix</sup>	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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