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4′-Phenyl-2,2′:6′,2″-terpyridine 1,1″-dioxide

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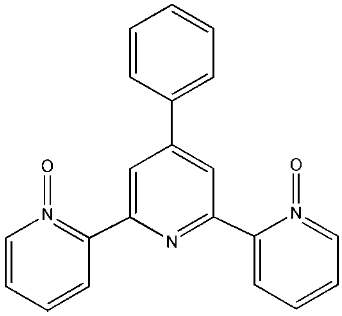
Key indicators: single-crystal X-ray study; T = 120 K; mean σ(C–C) = 0.002 Å; R factor = 0.045; wR factor = 0.126; data-to-parameter ratio = 15.2.

The title compound, $C_{21}H_{15}N_3O_2$, crystallizes with the molecules positioned on twofold rotation axes. Two crystallographically unique intermolecular C—H···O—N contacts produce a complex network of hydrogen bonds that assist in the stabilization of the crystal structure.

Related literature

For general background, see: Green (1974); Desiraju (1996); McKay *et al.* (2004); Steiner (1997); Taylor & Kennard (1982). For related structures, see: Constable *et al.* (1992); Thummel & Jahng (1985). For related literature, see: Allen (2002); Desiraju & Steiner (1999).



Experimental

Crystal data

$C_{21}H_{15}N_3O_2$
M_r = 341.36
Monoclinic, $C2/c$
a = 19.1173 (8) Å
b = 10.9251 (5) Å
c = 7.7581 (3) Å
β = 93.416 (2)°
V = 1617.47 (12) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.09 mm^{-1}
T = 120 (2) K
0.10 × 0.08 × 0.05 mm

Data collection

Nonius KappaCCD diffractometer
Absorption correction: multi-scan (*SORTAV*; Blessing, 1995)
T_{min} = 0.991, T_{max} = 0.995
7527 measured reflections
1843 independent reflections
1329 reflections with $I > 2\sigma(I)$
R_{int} = 0.112

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.045
$wR(F^2)$ = 0.126
S = 1.01
1843 reflections
121 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.26 e Å^{-3}
$\Delta\rho_{min}$ = −0.28 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
C2—H2···O1^{ii}	0.95	2.30	3.1382 (18)	147
C10—H10···O1^{iii}	0.95	2.35	3.2939 (19)	170

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

Data collection: *COLLECT* (Nonius, 2000); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *SCALEPACK* and *DENZO* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: RN2022).

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supplementary materials

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4'-Phenyl-2,2':6',2''-terpyridine 1,1''-dioxide

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Comment

The title molecule lies on a crystallographic twofold axis which passes through N(2), C(8), C(9) and C(12) atoms (see Fig. 1). The compound contains weak intermolecular C—H···O hydrogen bonds which are gaining more attention in the field of crystal engineering and their significance has been reported for numerous crystal structures (Green, 1974; Taylor & Kennard, 1982; Desiraju, 1996; Steiner, 1997; McKay *et al.*, 2004).

The aryl H atoms participate in C—H···O hydrogen bonds because of the electronic influence of the corresponding sp^2 C_{aryl} atom. The crystal structure of the compound was analysed to understand the hydrogen-bond preferences of C—H···O—N interactions. Terpyridine compounds are well represented in the Cambridge Structural Database (Allen, 2002), due to their excellent chelating and favorable hydrogen-bond-acceptor ability. Introduction of two N-oxide functionalities to the phenylterpyridine framework, provides an opportunity to explore the interdependency of two strong acceptors and molecular alignment.

The compound adopts a conformation that results from the twist about each pyridine–pyridine bond [N1—C5—C6—N2 = 128.91 (12)°]. This conformation is less skewed than that in the terpyridine trioxide [76.8 (2)°] (McKay *et al.*, 2004), presumably due to a more sterically favorable environment of the central pyridine fragment. Other selected geometric parameters are given in Table 1.

The supramolecular motifs observed in the structure of (I) are influenced by the construction of non-bonded contacts (Table 2) as the edges of the compound (I) are constituted exclusively with O atoms and C—H groups and it is to be expected that weak C—H···O hydrogen bonds will be present in the crystal structure (Steiner, 1997; Desiraju & Steiner, 1999). In the compound, C2 and C10 form these hydrogen bonds with O1 and C—H····O1—N1 contacts link neighboring terpyridine molecules (see Fig. 2).

Experimental

Phenyl terpyridine was prepared according to the method described in the literature (Constable *et al.*, 1992). Then oxygenation of the phenyl terpyridine was carried out by the following way: the 3-chloroperbenzoic acid (1.7257 g, 10 mmol, 60% pure) was added to a mixture of 4'-phenyl-2':6',2''- terpyridine (1.0315 g, 3 mmol) and CH_2Cl_2 (50 ml). After stirring overnight, the mixture was washed with 10% Na_2CO_3 solution (twice with 30 ml) and water (30 ml), dried ($MgSO_4$) and evaporated yielding phenylterpyridine dioxide as a white compound (Thummel & Jahng, 1985). The phenylterpyridine dioxide powder was dissolved in boiling absolute ethanol, concentrated and left for crystallization. Colorless crystals were obtained after one week.

Refinement

The H atoms were geometrically placed (C—H = 0.95 Å) and refined as riding with $U_{iso}(H) = 1.2U_{eq}$(carrier). The mosaicity of the crystal was high and it did not diffract well so the R_{int} is high.

Figures

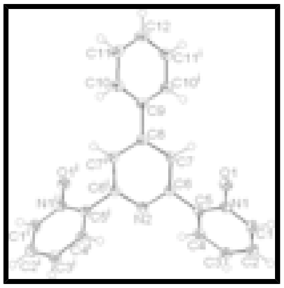

Fig. 1. View of the molecular structure of (I) showing 50% dispalcement ellipsoids (arbitrary spheres for the H atoms). Symmetry code: (i) −*x*, −*y*, −*z*.

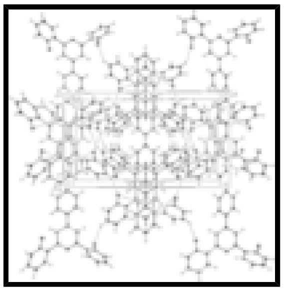

Fig. 2. The unit-cell packing of (I) viewed along the *b* axis. Dashed lines indicate the hydrogen bonding interactions.

4'-Phenyl-2,2':6',2''-terpyridine 1,1''-dioxide

Crystal data

$C_{21}H_{15}N_3O_2$	$F_{000} = 712$
$M_r = 341.36$	$D_x = 1.402$ Mg m^{-3}
Monoclinic, *C*2/*c*	Mo *K*α radiation $\lambda = 0.71073$ Å
Hall symbol: -C 2yc	Cell parameters from 1843 reflections
$a = 19.1173$ (8) Å	$\theta = 2.9$–27.5°
$b = 10.9251$ (5) Å	$\mu = 0.09$ mm^{-1}
$c = 7.7581$ (3) Å	$T = 120$ (2) K
$\beta = 93.416$ (2)°	Block, colorless
$V = 1617.47$ (12) Å^3	0.10 × 0.08 × 0.05 mm
$Z = 4$	

Data collection

Nonius KappaCCD diffractometer	1843 independent reflections
Radiation source: fine-focus sealed tube	1329 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.112$

T = 120(2) K	θ_{max} = 27.5°
ω and φ scans	θ_{min} = 3.4°
Absorption correction: multi-scan (SORTAV; Blessing, 1995)	$h = -24 \rightarrow 24$
T_{min} = 0.991, T_{max} = 0.995	$k = -14 \rightarrow 13$
7527 measured reflections	$l = -10 \rightarrow 10$

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.045$	$w = 1/[\sigma^2(F_o^2) + (0.0586P)^2 + 0.3346P]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.126$	$(\Delta/\sigma)_{max} < 0.001$
S = 1.01	$\Delta\rho_{max}$ = 0.26 e Å^{-3}
1843 reflections	$\Delta\rho_{min}$ = −0.28 e Å^{-3}
121 parameters	Extinction correction: SHELXL97, $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Primary atom site location: structure-invariant direct methods	Extinction coefficient: 0.0051 (11)
Secondary atom site location: difference Fourier map	

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 $F^2 > 2\text{sigma}(F^2)$ 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	$U_{iso}*/U_{eq}$
O1	0.18038 (6)	0.62710 (9)	0.09623 (13)	0.0263 (3)
N1	0.18001 (6)	0.71228 (11)	0.21502 (15)	0.0208 (3)
N2	0.0000	0.71614 (14)	0.2500	0.0185 (4)
C1	0.23682 (8)	0.78705 (14)	0.2399 (2)	0.0256 (4)
H1	0.2760	0.7756	0.1718	0.031*
C2	0.23843 (8)	0.87827 (14)	0.3610 (2)	0.0288 (4)
H2	0.2784	0.9297	0.3761	0.035*
C3	0.18193 (9)	0.89553 (13)	0.4611 (2)	0.0285 (4)
H3	0.1830	0.9568	0.5481	0.034*
C4	0.12369 (8)	0.82145 (13)	0.43189 (19)	0.0240 (4)

H4	0.0838	0.8338	0.4972	0.029*
C5	0.12276 (7)	0.72989 (13)	0.30924 (18)	0.0193 (4)
C6	0.05943 (7)	0.65209 (13)	0.27456 (16)	0.0185 (3)
C7	0.06210 (7)	0.52497 (12)	0.27623 (17)	0.0187 (3)
H7	0.1057	0.4838	0.2950	0.022*
C8	0.0000	0.45848 (18)	0.2500	0.0179 (4)
C9	0.0000	0.32240 (18)	0.2500	0.0193 (5)
C10	−0.05106 (8)	0.25744 (13)	0.15219 (18)	0.0223 (4)
H10	−0.0866	0.3003	0.0860	0.027*
C11	−0.05025 (8)	0.13022 (13)	0.15108 (19)	0.0259 (4)
H11	−0.0846	0.0869	0.0816	0.031*
C12	0.0000	0.0657 (2)	0.2500	0.0282 (5)
H12	0.0000	−0.0213	0.2500	0.034*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0277 (7)	0.0246 (6)	0.0269 (6)	0.0017 (4)	0.0051 (4)	−0.0043 (4)
N1	0.0209 (7)	0.0194 (7)	0.0219 (6)	0.0004 (5)	−0.0004 (5)	0.0039 (5)
N2	0.0182 (9)	0.0199 (9)	0.0171 (8)	0.000	0.0001 (7)	0.000
C1	0.0195 (8)	0.0278 (9)	0.0294 (8)	−0.0031 (6)	−0.0003 (6)	0.0076 (7)
C2	0.0252 (9)	0.0247 (8)	0.0353 (9)	−0.0066 (6)	−0.0084 (7)	0.0082 (7)
C3	0.0318 (10)	0.0197 (8)	0.0329 (8)	−0.0008 (6)	−0.0080 (7)	−0.0013 (7)
C4	0.0240 (8)	0.0220 (8)	0.0258 (8)	0.0024 (6)	−0.0014 (6)	−0.0005 (6)
C5	0.0185 (8)	0.0177 (7)	0.0213 (7)	0.0011 (6)	−0.0013 (6)	0.0043 (6)
C6	0.0203 (8)	0.0186 (7)	0.0168 (7)	0.0001 (6)	0.0020 (5)	0.0001 (6)
C7	0.0178 (8)	0.0192 (7)	0.0191 (7)	0.0024 (5)	0.0011 (5)	0.0011 (5)
C8	0.0208 (11)	0.0182 (10)	0.0148 (9)	0.000	0.0023 (7)	0.000
C9	0.0237 (11)	0.0163 (10)	0.0184 (9)	0.000	0.0055 (8)	0.000
C10	0.0252 (9)	0.0205 (8)	0.0214 (8)	0.0009 (6)	0.0024 (6)	0.0005 (6)
C11	0.0309 (9)	0.0217 (8)	0.0254 (8)	−0.0058 (6)	0.0029 (6)	−0.0035 (6)
C12	0.0372 (14)	0.0170 (10)	0.0312 (11)	0.000	0.0097 (10)	0.000

Geometric parameters (Å, °)

O1—N1	1.3100 (15)	C6—C7	1.3897 (19)
N1—C1	1.3634 (19)	C7—C8	1.3963 (17)
N1—C5	1.3655 (19)	C7—H7	0.9500
N2—C6	1.3383 (16)	C8—C7^{i}	1.3963 (17)
N2—C6^{i}	1.3384 (16)	C8—C9	1.487 (3)
C1—C2	1.369 (2)	C9—C10	1.3943 (18)
C1—H1	0.9500	C9—C10^{i}	1.3943 (18)
C2—C3	1.381 (2)	C10—C11	1.390 (2)
C2—H2	0.9500	C10—H10	0.9500
C3—C4	1.384 (2)	C11—C12	1.3861 (19)
C3—H3	0.9500	C11—H11	0.9500
C4—C5	1.380 (2)	C12—C11^{i}	1.3861 (19)
C4—H4	0.9500	C12—H12	0.9500

C5—C6	1.4905 (19)		
O1—N1—C1	119.17 (13)	N2—C6—C5	113.65 (12)
O1—N1—C5	120.98 (12)	C7—C6—C5	122.63 (12)
C1—N1—C5	119.81 (13)	C6—C7—C8	119.22 (13)
C6—N2—C6^{i}	116.95 (16)	C6—C7—H7	120.4
N1—C1—C2	121.22 (15)	C8—C7—H7	120.4
N1—C1—H1	119.4	C7—C8—C7^{i}	117.30 (18)
C2—C1—H1	119.4	C7—C8—C9	121.35 (9)
C1—C2—C3	119.97 (14)	C7^{i}—C8—C9	121.35 (9)
C1—C2—H2	120.0	C10—C9—C10^{i}	118.81 (19)
C3—C2—H2	120.0	C10—C9—C8	120.60 (9)
C2—C3—C4	118.46 (14)	C10^{i}—C9—C8	120.60 (9)
C2—C3—H3	120.8	C11—C10—C9	120.31 (14)
C4—C3—H3	120.8	C11—C10—H10	119.8
C5—C4—C3	120.94 (15)	C9—C10—H10	119.8
C5—C4—H4	119.5	C12—C11—C10	120.85 (14)
C3—C4—H4	119.5	C12—C11—H11	119.6
N1—C5—C4	119.57 (14)	C10—C11—H11	119.6
N1—C5—C6	119.43 (13)	C11^{i}—C12—C11	118.85 (19)
C4—C5—C6	120.98 (13)	C11^{i}—C12—H12	120.6
N2—C6—C7	123.65 (13)	C11—C12—H12	120.6
O1—N1—C1—C2	179.18 (12)	N1—C5—C6—C7	54.03 (18)
C5—N1—C1—C2	1.6 (2)	C4—C5—C6—C7	−127.69 (15)
N1—C1—C2—C3	0.3 (2)	N2—C6—C7—C8	0.43 (19)
C1—C2—C3—C4	−2.0 (2)	C5—C6—C7—C8	177.19 (10)
C2—C3—C4—C5	2.0 (2)	C6—C7—C8—C7^{i}	−0.20 (9)
O1—N1—C5—C4	−179.16 (12)	C6—C7—C8—C9	179.80 (9)
C1—N1—C5—C4	−1.6 (2)	C7—C8—C9—C10	−150.68 (9)
O1—N1—C5—C6	−0.85 (19)	C7^{i}—C8—C9—C10	29.32 (9)
C1—N1—C5—C6	176.70 (12)	C7—C8—C9—C10^{i}	29.32 (9)
C3—C4—C5—N1	−0.2 (2)	C7^{i}—C8—C9—C10^{i}	−150.68 (9)
C3—C4—C5—C6	−178.46 (13)	C10^{i}—C9—C10—C11	−0.80 (10)
C6^{i}—N2—C6—C7	−0.22 (9)	C8—C9—C10—C11	179.20 (10)
C6^{i}—N2—C6—C5	−177.24 (12)	C9—C10—C11—C12	1.6 (2)
N1—C5—C6—N2	−128.91 (12)	C10—C11—C12—C11^{i}	−0.81 (10)
C4—C5—C6—N2	49.37 (17)		

Symmetry codes: (i) −*x*, *y*, −*z*+1/2.

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C2—H2···O1^{ii}	0.95	2.30	3.1382 (18)	147
C10—H10···O1^{iii}	0.95	2.35	3.2939 (19)	170

Symmetry codes: (ii) −*x*+1/2, *y*+1/2, −*z*+1/2; (iii) −*x*, −*y*+1, −*z*.

Fig. 1

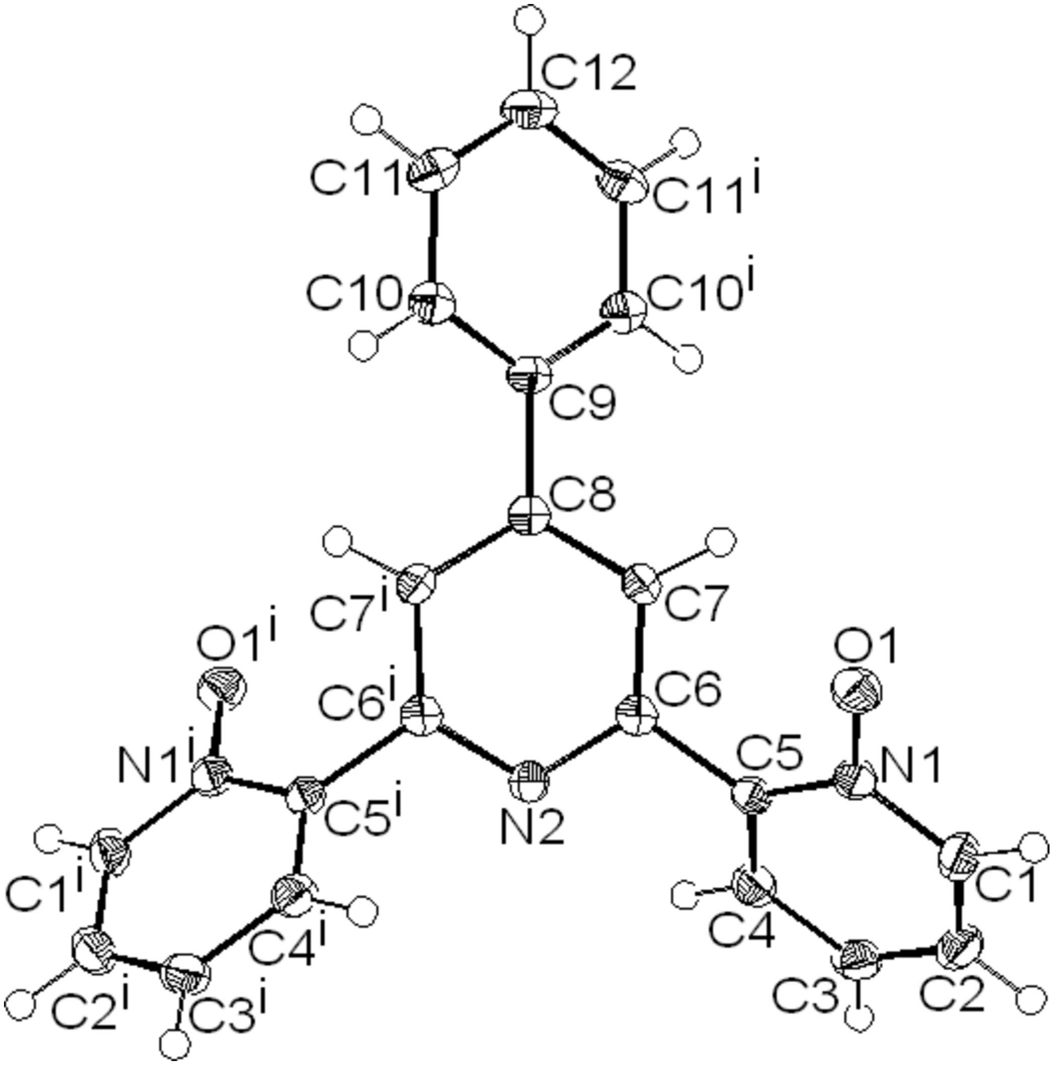
C12
C11
C11i
C10
C10i
C9
C8
C7i
C7
O1i
O1
C6i
C6
C5
N1
N1i
C5i
N2
C1i
C1
C4i
C4
C2i
C3i
C3
C2

Fig. 2