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Ethyl 5,5″-dimethyl-2,2′;6′,2″-terpyridine-4′-carboxylate

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Key indicators

Single-crystal X-ray study
T = 173 K
Mean σ(C–C) = 0.002 Å
R factor = 0.049
wR factor = 0.149
Data-to-parameter ratio = 18.2

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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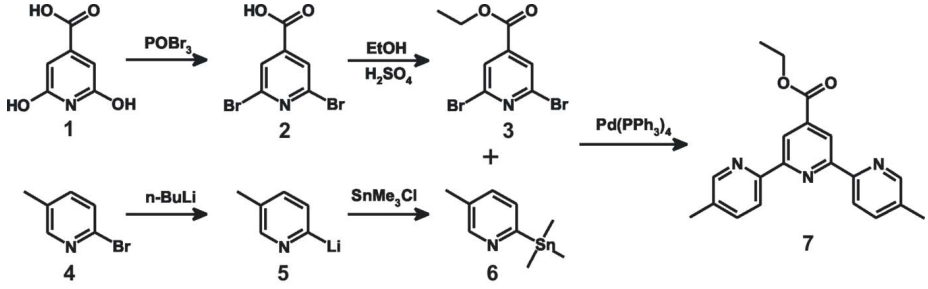
The title compound, $C_{20}H_{19}N_3O_2$, was synthesized by Stille coupling of ethyl 2,6-dibromoisonicotinate and 2-trimethylstannyl-5-methylpyridine. The three pyridine rings in the molecule are coplanar and the crystal packing reveals π–π stacking interactions between these conjugated aromatic rings with a distance between the mean planes of 3.494 Å.

Comment

2,2′;6′,2″-Terpyridine is a well known chelating ligand for a wide variety of transition metal ions (Hofmeier & Schubert, 2004). This supramolecular binding motif has been applied for the assembly of, for example, metallodendrimers (Constable, 1997) and metallosupramolecular polymers (Schubert & Eschbaumer, 2002; Andres & Schubert, 2004). The synthesis of functionalized 2,2′:6′,2″-terpyridines has been reviewed in recent years by Cargill Thompson (1997), Fallahpour (2003) and Heller & Schubert (2003). The crystal structure of the unsubstituted 2,2′:6′,2″-terpyridine was reported by Bessel *et al.* (1992). Subsequently, crystal structures of 4′-substituted 2,2′:6′,2″-terpyridines, such as 4′-vinyl-2,2′:6′,2″-terpyridine (Liu *et al.*, 2000), 4′-butoxy- and 4′-dodecyloxy-2,2′:6′,2″-terpyridine (Andres *et al.*, 2003), and 4′-(5-isocyanatopentyloxy)-2,2′;6′,2″-terpyridine (Hoogenboom *et al.*, 2004), have been reported. However, only a few crystal structures of 6,6″-substituted 2,2′:6′,2″-terpyridines have been described in the literature, namely 6-[(1*S*)-*endo*]-(−)-bornyloxy-2,2′:6′,2″-terpyridine, 6-[(1*S*)-*endo*]-(−)-bornyloxy-6″-methyl-2,2′:6′,2″-terpyridine (Baum *et al.*, 2000), 4,4-difluoro-8-(6‴-methyl-2′,2″:6″,2‴-terpyridin-6′-yl)-1,3,5,7-tetramethyl-2,4-diethyl-4-bora-3a,4a-diaza-*s*-indacene (Goze *et al.*, 2003), 6,6″-bis(trimethylsilylethynyl)-2,2′:6′,2″-terpyridine and 6,6″-bis(trimethylsilylethynyl)-4′-phenyl-2,2′:6′,2″-terpyridine (Khan *et al.*, 2002). To the best of our knowledge, the crystal structure of this latter compound is the only structure reported for a 2,2′:6′,2″-terpyridine with substituents on all three rings.



We report here the crystal structure of another 2,2′:6′,2″-terpyridine with three substituents, namely the title

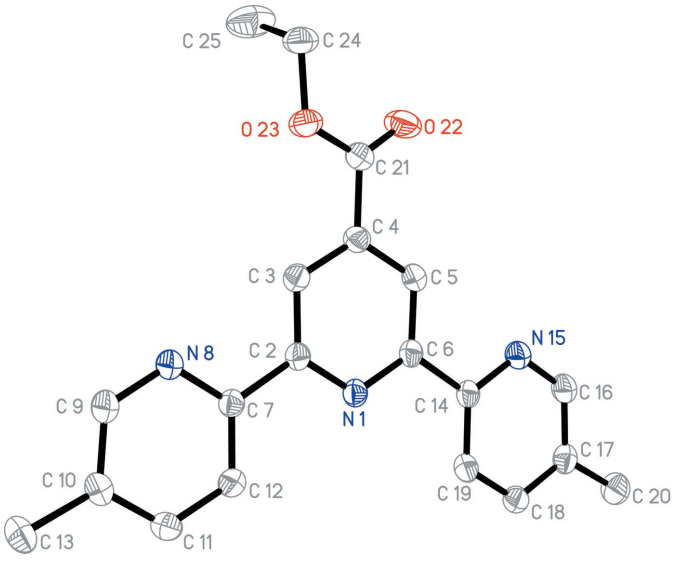


Figure 1
The structure of (7), with displacement ellipsoids shown at the 50% probability level. For clarity, H atoms have been omitted.

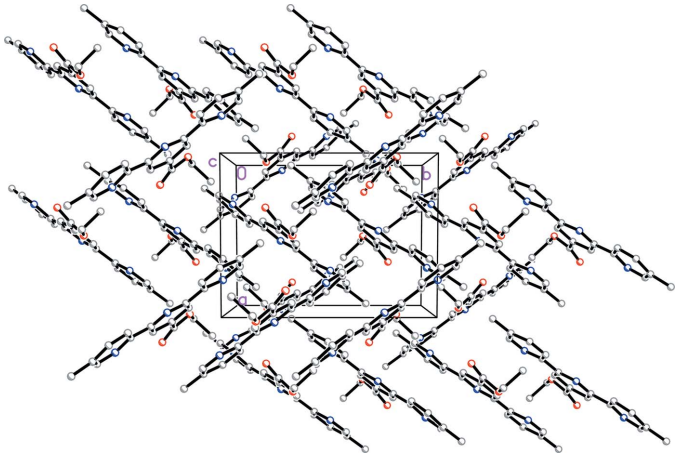


Figure 2
Projection of the structure along [001]. For clarity, H atoms have been omitted.

compound, (7). The molecular structure of (7) is shown in Fig. 1. The three rings of the terpyridine unit, N1/C2–C6, C7/N8/C9–C12 and C14/N15/C16–C19, are coplanar. The plane through the terpyridine unit makes an angle to the carboyxylic ester group (C21/O22/O23) of 10.99 (4)°. All bond lengths and angles can be regarded as normal. The crystal packing reveals π–π stacking interactions between the conjugated aromatic rings in the structure, with a distance between the mean planes of 3.494 Å (Fig. 2).

Experimental

Compound (7) was synthesized starting from 2,6-dihydroxyisonicotinic acid, (1), and 2-bromo-5-methylpyridine, (4), following a modified literature procedure (Fallahpour, 2000; Heller & Schubert, 2002). Compound (1) was converted into 2,6-dibromoisonicotinic acid ethyl ester, (3), *via* 2,6-dibromoisonicotinic acid, (2). 2-Bromo-5-methylpyridine was lithiated, resulting in (5), and converted into 2-trimethylstannyl-5-methylpyridine, (6), by the addition of trimethylstannylchloride (in the literature method 2-tributylstannyl-5-methylpyridine was used). Compounds (3) and (6) were coupled *via* a $Pd(PPh_3)_4$-catalysed Stille coupling, resulting in the title compound (7), which crystallized as single crystals by slow evaporation of a $CDCl_3$ solution. The reaction scheme of the synthesis is shown above.

Crystal data

$C_{20}H_{19}N_3O_2$
M_r = 333.38
Monoclinic, $P2_1/n$
a = 9.0892 (5) Å
b = 11.8780 (6) Å
c = 15.8131 (8) Å
β = 97.975 (1)°
V = 1690.70 (15) Å^3
Z = 4
D_x = 1.310 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 5732 reflections
θ = 4.9–56.5°
μ = 0.09 mm^{-1}
T = 173 (2) K
Irregular fragment, colourless
0.56 × 0.41 × 0.26 mm

Data collection

Bruker SMART CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.953, T_{max} = 0.978
11535 measured reflections
4169 independent reflections
3408 reflections with $I > 2\sigma(I)$
R_{int} = 0.028
θ_{max} = 28.3°
$h = -12 \rightarrow 12$
$k = -15 \rightarrow 15$
$l = -11 \rightarrow 21$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.049
$wR(F^2)$ = 0.149
S = 1.06
4169 reflections
229 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0991P)^2 + 0.1562P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.006
$\Delta\rho_{max}$ = 0.33 e Å^{-3}
$\Delta\rho_{min}$ = −0.37 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

C10—C13	1.5066 (15)	C21—O23	1.3365 (14)
C17—C20	1.5070 (16)	O23—C24	1.4580 (14)
C21—O22	1.2003 (14)		
N1—C2—C7	116.99 (9)	O23—C21—C4	111.74 (9)
N1—C6—C14	116.79 (9)	C21—O23—C24	117.03 (9)
O22—C21—O23	124.52 (11)	O23—C24—C25	110.32 (11)
O22—C21—C4	123.74 (11)		
N1—C2—C7—N8	−178.07 (9)	O22—C21—O23—C24	2.06 (18)
N1—C6—C14—N15	176.78 (9)	C21—O23—C24—C25	91.01 (14)
C3—C4—C21—O22	−167.76 (12)		

H atoms were located in difference Fourier maps and refined with a riding model, with C—H distances of 0.95 (aromatic H), 0.98 (methyl H) and 0.99 Å (methylene H), and with U_{iso}(H) = 1.2U_{eq}(C) for aromatic and methylene H, or 1.5U_{eq}(C) for methyl H.

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINT* (Bruker, 1997); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1998); software used to prepare material for publication: *SHELXTL*.

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