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# Diethyl 4-(4-*tert*-butylphenyl)pyridine-2,6-dicarboxylate

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**Key indicators**

Single-crystal X-ray study
*T* = 100 K
Mean σ(C–C) = 0.003 Å
*R* factor = 0.059
*wR* factor = 0.176
Data-to-parameter ratio = 14.4

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



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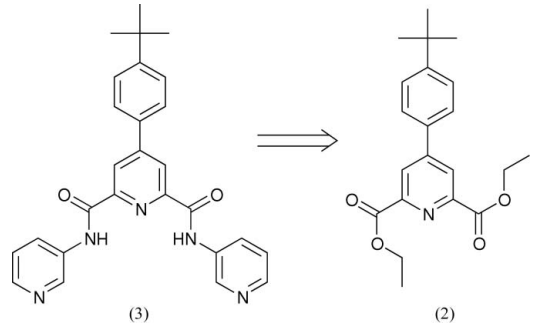
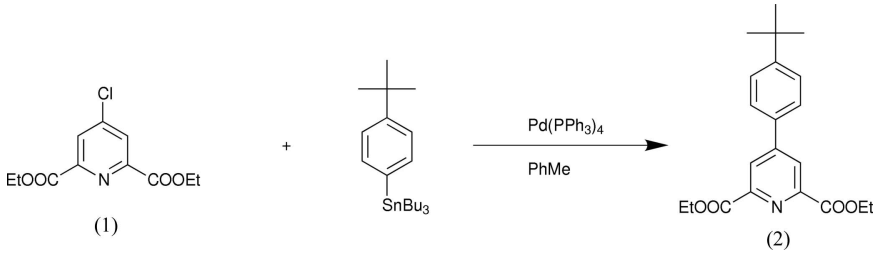
The title crystal structure, $C_{21}H_{25}NO_4$, is stabilized by π-stacking interactions between inversion-related pyridyl groups with a ring centroid-to-centroid distance of 3.450 (14) Å. In addition, non-polar *tert*-butyl groups face each other, forming alternating polar and non-polar layers.

## Comment

Flexible self-assembled supramolecular structures are of particular interest given that the binding of guest molecules into receptors follows an induced-fit mechanism. Weak interactions for guest binding is thus favored, and metalloreceptors may bind the substrate through their primary coordination sphere (i.e. bond between metal and substrate), their secondary coordination sphere (i.e. bond between ligand and substrate), or a combination of both.




Metalloreceptors require organic ligands with metal-binding units, a rigid spacer and hydrogen-bonding groups. An appropriate motif is the diamidopyridine molecule (Baer *et al.*, 2002). The design of a ligand is an important step as the geometry and the reactivity of the metalloreceptor determine its ability to bind the substrate *e.g.* carboxylic acid groups can be used to connect various photo-active sub-units to transition metal ions (Cooke & Hanan, 2007). To enhance the solubility of carboxylic acid pyridine-based compounds, we grafted solubilizing groups such as *tert*-buytlphenyl to the 4-position of a central pyridine group. The title compound, (2), was

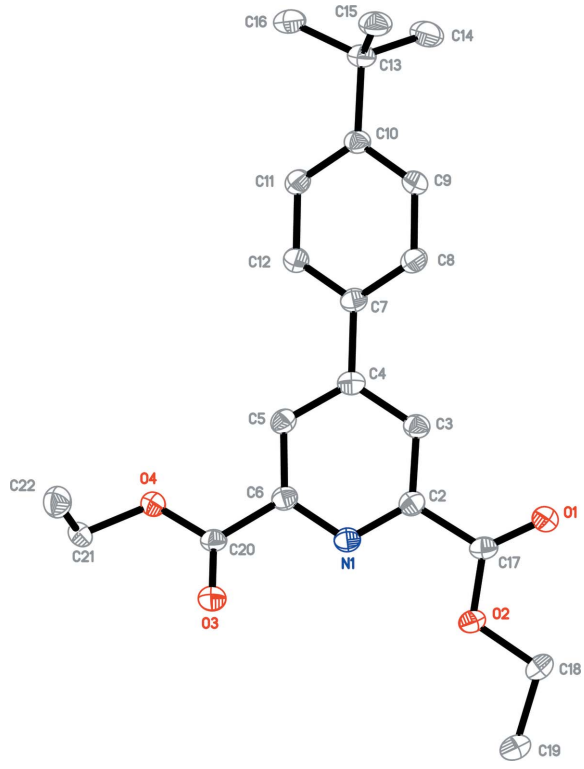



**Figure 1**
The molecular structure of (2), showing displacement ellipsoids drawn at the 50% probability level. H atoms have been omitted for clarity.

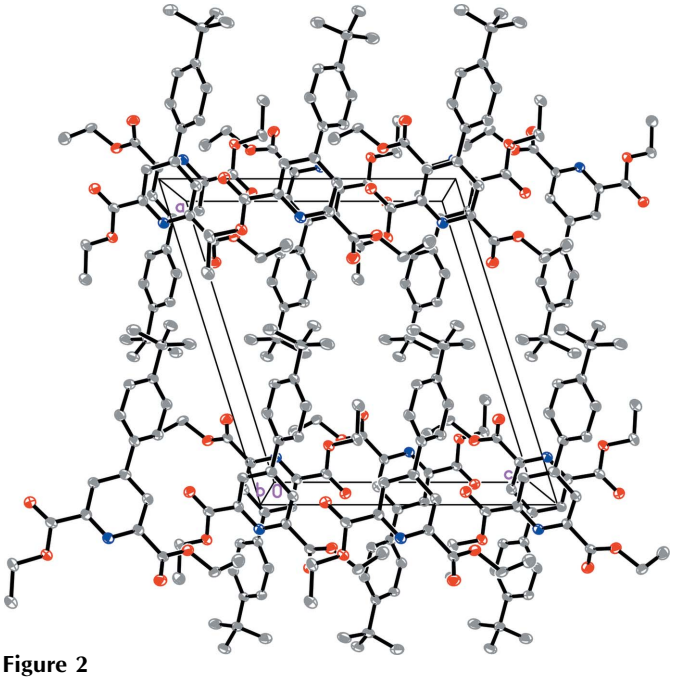


**Figure 2**
Partial packing plot of (2), projected on to the *ac* plane.

synthesized as a stable intermediate in our attempt to enhance the solubility of dicarboxylic-acid-functionalized polypyridine ligands. Metal ions can direct the self-assembly of tridentate pyridine-based ligands into large supramolecular structures for molecular-recognition purposes.

The molecular structure of the title compound (2) (Fig. 1) is an intermediate in the synthesis of the tridentate ligand (3). We prepared this diethyl ester (2) as the dicarboxylic acid analog did not give crystals suitable for X-ray diffraction. One of the ester groups is in an extended conformation and almost planar with the pyridyl ring, making a dihedral angle of 5.51 (11) Å between the planes formed by atoms C2/C17/O1/O2/C18/C19 and N1/C6/C5/C4/C3/C2. The other ester group has a coiled conformation defined by the C20—O4—C21—C22 torsion angle of 86.4 (2)°, the carbonyl group being slightly out of the pyridine ring plane as described by N1—C6—C20—O3 = 22.4 (3)°. These conformations may be necessary in terms of the formation of weak intermolecular C—H···O hydrogen bonds (Table 1). The benzene ring is twisted from the pyridyl ring by 34.0 (3)°, as described by the C5—C4—C7—C12 torsion angle. The crystal structure is stabilized by significant $\pi\cdots\pi$ stacking interactions with $Cg\cdots Cg(2-x,-y,1-z)$ = 3.450 (14) Å and a perpendicular distance of 3.198 Å (where *Cg* is the centroid of ring atoms N1,C2–C6). In addition, *tert*-butyl groups face each other, forming alternating polar and non-polar layers (see Fig. 2).

## Experimental

$Pd(PPh_3)_4$ (0.144 g, 0.125 mmol) was added to 4-chloropyridine-2,6-dicarboxylic acid diethyl ester (1) (0.644 g, 2.5 mmol) in a flame-dried, argon-charged, two-necked flask (100 ml). Toluene (30 ml) and tributyl-(4-*tert*-butylphenyl)tin (1.041 g, 2.46 mmol) were added by syringe. The mixture was heated at 373–383K for 38 h, during which time KF(aq. sat.) (10 ml) was added. The mixture was stired at r.t. for 3 h before diethyl ether (25 ml) and water (25 ml) were added. The resulting mixture was extracted with diethyl ether (3×25 ml). The organic phase was dried over $Na_2SO_4$ and $Na_2CO_3$. The solvents were then evaporated under reduced pressure and the solid residue was purified by column chromatography using silica gel (eluant 3:1 hexane/ethyl acetate). The title compound (2) was isolated as a colorless crystalline solid (0.814 g, 92%). These crystals were suitable for X-ray diffraction measurements.

*Crystal data*

$C_{21}H_{25}NO_4$
$M_r$ = 355.42
Monoclinic, $P2_1/c$
$a$ = 13.857 (2) Å
$b$ = 12.0094 (17) Å
$c$ = 12.0553 (17) Å
$\beta$ = 107.368 (7)°
$V$ = 1914.7 (5) Å$^3$
$Z$ = 4
Cu $K\alpha$ radiation
$\mu$ = 0.69 mm$^{-1}$
$T$ = 100 (2) K
0.40 × 0.24 × 0.20 mm

*Data collection*

Bruker SMART 6000 diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min}$ = 0.750, $T_{max}$ = 0.875
23628 measured reflections
3456 independent reflections
2627 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.088

*Refinement*

$R[F^2 > 2\sigma(F^2)]$ = 0.059
$wR(F^2)$ = 0.176
$S$ = 1.02
3456 reflections
240 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.36 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.31 e Å$^{-3}$

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| C8—H8···O3$^{i}$ | 0.95 | 2.52 | 3.463 (3) | 175 |
| C12—H12···O1$^{ii}$ | 0.95 | 2.46 | 3.406 (3) | 174 |
| C21—H21$B$···N1$^{ii}$ | 0.99 | 2.58 | 3.287 (3) | 128 |

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

H atoms were positioned geometrically (C—H 0.95–0.99 Å) and were included in the refinement in the riding-model approximation with $U_{iso}$(H) = 1.2$U_{eq}$(C) or 1.5$U_{eq}$($C_{methyl}$).

Data collection: *SMART* (Bruker, 2003); cell refinement: *SAINT* (Bruker, 1999); 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, 1997); software used to prepare material for publication: *UdMX* (local program).

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