organic papers

Diethyl 2,6-dimethylpyridine-3,5-dicarboxylate

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The molecular structure of the title compound, $C_{13}H_{17}NO_4$, has no symmetry plane because one C atom of the ethyl group lies out of the plane defined by the other non-H atoms. In the crystal structure, the molecules stack along the a axis. Symmetry-related molecules are linked by a C—H···O hydrogen bond, forming zigzag chains extending in the b-axis direction.

Comment

Dihydropyridine compounds are calcium ion channel blockers and the use of these compounds is generally beneficial (Böcker *et al.*, 1986). Aromatization of Hantzsch 1,4-dihydropyridines (1,4-DHP) has attracted considerable attention in recent years, essentially since the discovery that the metabolism of these drugs involves an oxidation step (Eynde *et al.*,1995). Here we describe the synthesis (Lu *et al.*, 2001) and crystal structure of the title compound, (I).

(I)
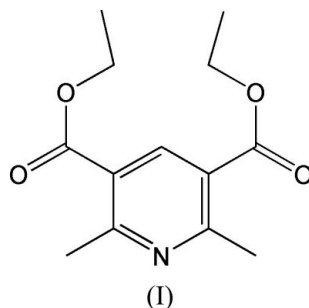
The molecular structure of the compound (I) is shown in Fig. 1 and selected geometric parameters are given in Table 1. All of the non-H atoms in (I) lie almost in the same plane, except atom C10 which is out of the plane with a C8—O2—C9—C10 torsion angle of 123.2 (17)°. This is probably because of the disorder of the ethyl group, and for this reason the molecule has no symmetry plane.

In the crystal structure of (I), the molecules stack along the a axis and are linked by C—H···O hydrogen bonds, forming polymer chains extending in the b-axis direction (Table 2, Fig. 2).

Experimental

The title compound, (I) was prepared according to the literature procedure of Lu *et al.* (2001). A mixture of diethyl 2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate, ferric chloride hexahydrate, acetic acid and water was heated at reflux for 1 h. After neutralization with an aqueous solution of sodium bicarbornate and extraction with chloroform, the title compound was obtained (yield 52%; m.p. 343–

344 K). Single crystals, suitable for X-ray diffraction analysis, were obtained by slow evaporation of an ethanol solution. IR (KBr, ν cm^{-1}): 2979, 2932, 1721, 1591, 1442, 1367, 1296, 1223, 1120, 1043, 771, 698.

Crystal data

$C_{13}H_{17}NO_4$	$D_x = 1.212$ Mg m^{-3}
$M_r = 251.28$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 1328
$a = 4.593$ (2) Å	reflections
$b = 15.950$ (9) Å	$\theta = 2.5–23.6°$
$c = 18.795$ (10) Å	$\mu = 0.09$ mm^{-1}
$\beta = 90.656$ (9)°	$T = 294$ (2) K
$V = 1376.9$ (13) Å^3	Block, colorless
$Z = 4$	$0.24 \times 0.20 \times 0.16$ mm

Data collection

Bruker SMART CCD area-detector diffractometer	2427 independent reflections
	1158 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{int} = 0.046$
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)	$\theta_{max} = 25.0°$
	$h = -4 \rightarrow 5$
$T_{min} = 0.960$, $T_{max} = 0.986$	$k = -18 \rightarrow 12$
6854 measured reflections	$l = -22 \rightarrow 22$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0658P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.049$	$+ 0.2484P]$
$wR(F^2) = 0.155$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.00$	$(\Delta/\sigma)_{max} = 0.002$
2427 reflections	$\Delta\rho_{max} = 0.20$ e Å^{-3}
187 parameters	$\Delta\rho_{min} = -0.14$ e Å^{-3}
H-atom parameters constrained	

Table 1
Selected torsion angles (°).

C8—O2—C9—C10	123.2 (17)	C11—O4—C12—C13	178.7 (3)

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
C12—H12$B\cdots$O1^i	0.97	2.52	3.346 (4)	143

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

All H atoms were positioned geometrically and refined as riding atoms with C—H distances = 0.93–0.97 Å. For the aromatic and CH$_2$ H atoms U_{iso}(H) = 1.2U_e(C), and for the CH$_3$ H atoms U_{iso}(H) = 1.5U_{eq}(C). The ethyl group was found to be disordered over two orientations, with occupancies of 0.39 (2) and 0.61 (2).

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, 1997); software used to prepare material for publication: *SHELXTL*.
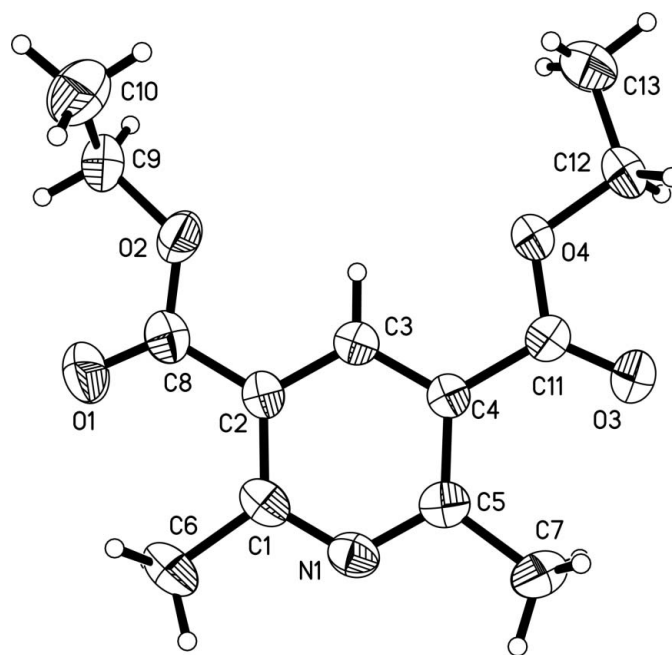
Figure 1
The molecular structure of compound (I), showing the atom-labeling scheme, with displacement ellipsoids drawn at the 35% probability level. Only the major component of the disordered ethyl group is shown.
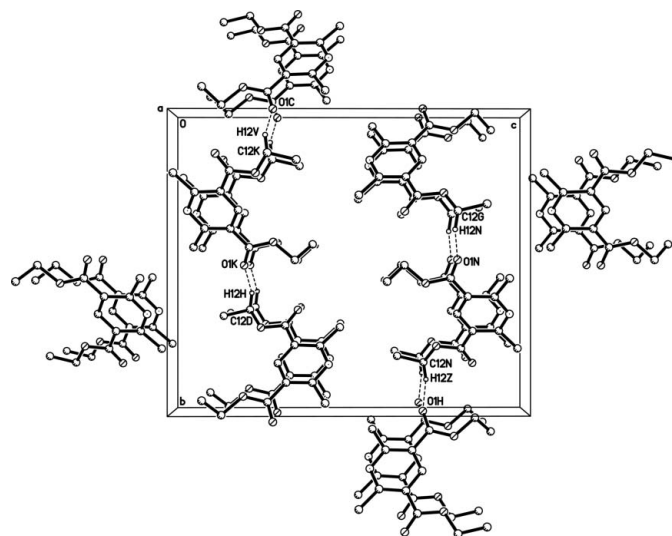

Figure 2
The crystal packing of compound (I), viewed along the *a* axis. Only the major component of the disordered ethyl group is shown. The C—H$\cdots$O hydrogen bonds are shown as dashed lines.

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