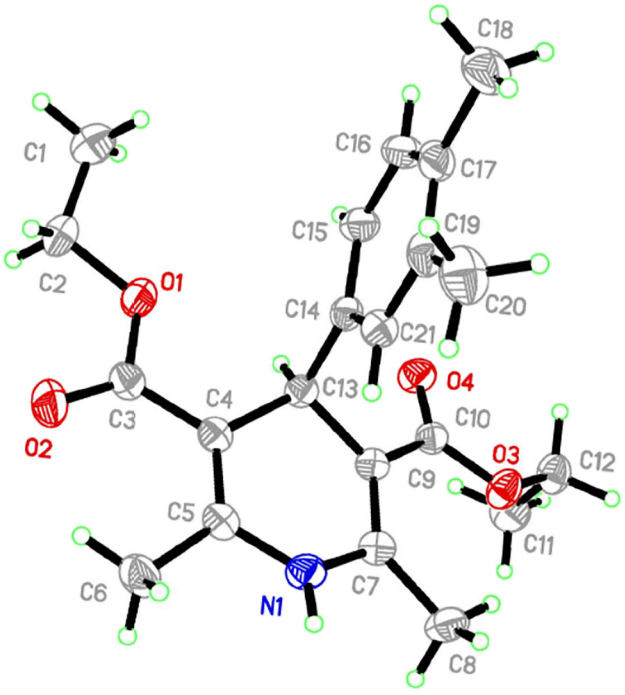
Yu Hai-Yan* and Zhang Li

The crystal structure of diethyl 4-(3,4-dimethylphenyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate, $C_{21}H_{27}NO_4$



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Abstract

$C_{21}H_{27}NO_4$, triclinic, $P\bar{1}$ (no. 2), a = 7.5904(17) Å, b = 10.394(2) Å, c = 12.651(3) Å, α = 73.270(4)°, β = 85.888(4)°, γ = 86.078(4)°, V = 952.2(4) Å^3, Z = 2, $R_{gt}(F)$ = 0.0469, $wR_{ref}(F^2)$ = 0.1545, T = 296(2) K.

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The molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

***Corresponding author: Yu Hai-Yan**, School of Biological and Chemical Engineering, Nanyang Institute of Technology, Nanyang 473004, China, E-mail: yuhaiyan06161979@163.com. https://orcid.org/0009-0001-3616-028X
Zhang Li, School of Biological and Chemical Engineering, Nanyang Institute of Technology, Nanyang 473004, China. https://orcid.org/0000-0003-1817-9056

Table 1: Data collection and handling.

Crystal:	Yellow block
Size:	0.32 × 0.28 × 0.21 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	0.09 mm^{-1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
θ_{max}, completeness:	25.2°, 99 %
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	4914, 3390, 0.019
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2430
$N(param)_{refined}$:	242
Programs:	Bruker [1], Olex2 [2], SHELX [3, 4]

1 Source of materials

All starting materials were of analytical grade and used without any further purification. The title compound was synthesized as follows: in 100 mL anhydrous ethanol, 2.0 mmol ethyl acetoacetate, 1.0 mmol ammonium acetate, and 1.0 mmol 3,4-dimethylbenzaldehyde were added and well-mixed. The mixture was heated at 333 K for 6 h, then naturally cooled to room temperature. A yellow precipitate was collected and recrystallized from 95 % ethanol, yield 54.6 % (based on 3-cyanobenzaldehyde). Yellow block crystals were obtained from the filtrate by recrystallization.

2 Experimental details

The structure was solved by Direct Methods with the SHELXS-2018 program. All H-atoms from C and the other atoms were positioned with idealized geometry and refined isotropically (U_{iso}(H) = 1.2 U_{eq}(C) or U_{eq}(N)) using a riding model with C–H = 0.930, 0.960 and 0.980 Å and N–H = 0.859 Å. An EXTI (0.047(7)) order was used in the refinement.

3 Comment

Since the discovery of pharmacological effects of this class of dimethyl or diethyl 4-phen-yl-2,6-dimethyl-1,4-dihydro-pyridine-3,5-dicarboxylate and their derivatives [5–8], they have been of

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
C1	0.0655 (3)	0.3890 (2)	0.65069 (18)	0.0574 (6)
H1A	−0.031640	0.416650	0.601915	0.069*
H1B	0.081518	0.460911	0.683326	0.069*
C2	0.2113 (2)	0.30030 (17)	0.51276 (14)	0.0401 (5)
C3	0.3800 (2)	0.26560 (17)	0.46236 (15)	0.0394 (4)
C4	0.5394 (2)	0.26966 (18)	0.50250 (15)	0.0442 (5)
C5	0.5809 (3)	0.3192 (2)	0.59744 (18)	0.0592 (6)
H5A	0.555182	0.414504	0.579574	0.089*
H5B	0.703869	0.300059	0.611666	0.089*
H5C	0.510194	0.274784	0.661979	0.089*
C6	0.6803 (2)	0.14524 (18)	0.38118 (16)	0.0437 (5)
C7	0.0209 (3)	0.2651 (2)	0.73958 (19)	0.0698 (7)
H7A	−0.012826	0.198189	0.707118	0.105*
H7B	−0.075362	0.285564	0.786540	0.105*
H7C	0.122186	0.231447	0.782503	0.105*
C8	0.5266 (2)	0.13893 (17)	0.33704 (15)	0.0410 (5)
C9	0.5154 (3)	0.05683 (19)	0.26161 (17)	0.0479 (5)
C10	0.3351 (3)	0.0063 (2)	0.1358 (2)	0.0656 (6)
H10A	0.333952	−0.090367	0.168012	0.079*
H10B	0.433434	0.025813	0.081277	0.079*
C11	0.1665 (3)	0.0579 (3)	0.0829 (2)	0.0734 (7)
H11A	0.159284	0.025925	0.019325	0.110*
H11B	0.161875	0.154413	0.060357	0.110*
H11C	0.069055	0.026621	0.134593	0.110*
C12	0.3653 (2)	0.22447 (18)	0.35771 (14)	0.0395 (4)
H12	0.261923	0.169661	0.368327	0.047*
C13	0.3345 (2)	0.34779 (18)	0.26094 (14)	0.0397 (5)
C14	0.1752 (3)	0.3753 (2)	0.21056 (16)	0.0501 (5)
H14	0.083784	0.317088	0.235965	0.060*
C15	0.1511 (3)	0.4884 (2)	0.12303 (17)	0.0576 (6)
H15	0.042452	0.505356	0.090732	0.069*
C16	0.2518 (4)	0.6988 (2)	−0.0157 (2)	0.0822 (8)
H16A	0.336182	0.695293	−0.075199	0.123*
H16B	0.265168	0.779062	0.005439	0.123*
H16C	0.134308	0.699396	−0.039392	0.123*
C17	0.2827 (3)	0.5776 (2)	0.08155 (16)	0.0551 (6)
C18	0.8540 (3)	0.0755 (2)	0.3625 (2)	0.0603 (6)
H18A	0.849415	−0.018823	0.399946	0.090*
H18B	0.946279	0.112741	0.390726	0.090*
H18C	0.877554	0.087822	0.284685	0.090*
C19	0.4435 (3)	0.5522 (2)	0.13239 (17)	0.0515 (5)
C20	0.5905 (3)	0.6453 (2)	0.0929 (2)	0.0747 (7)
H20A	0.611895	0.661443	0.014523	0.112*
H20B	0.695665	0.605568	0.129637	0.112*
H20C	0.558708	0.728964	0.108961	0.112*
C21	0.4649 (3)	0.43826 (19)	0.22067 (16)	0.0462 (5)
H21	0.572282	0.421891	0.254446	0.055*
N1	0.6865 (2)	0.22060 (16)	0.45422 (14)	0.0497 (4)
H1	0.788693	0.237931	0.470532	0.060*
O1	0.22443 (18)	0.36697 (14)	0.58762 (12)	0.0545 (4)
O2	0.06931 (17)	0.27366 (14)	0.48859 (11)	0.0525 (4)
O003	0.35445 (18)	0.07081 (14)	0.22038 (12)	0.0557 (4)
O004	0.6301 (2)	−0.01365 (17)	0.23405 (15)	0.0769 (5)

interest. To the best of our knowledge, only four results of methyl-substitution on 4-phenyl group have been reported, including dimethyl 4-(2-methylphenyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate [9], and dimethyl 4-(3-methylphenyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate [10], dimethyl 4-(4-methylphenyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate [10] and diethyl 4-(4-methylphenyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate [11]. However, the crystal structure of dimethyl-substitution on 4-phenyl group has not been reported.

As shown in the figure, the asymmetric unit consists of one 2,6-dimethyl-3,5-diethoxycarbonyl-1,4-dihydropyridine ring and one 3,4-dimethylphenyl group. A 1D chain is generated by the intermolecular hydrogen bond N1–H1A···O2. A 3D supramolecular structure is generated by this 1D chain and hydrogen bond C18–H18A···O2, C18–H18B···O2, and weak intermolecular interactions C7–H7B···π and C16–H16A···π. All bond lengths and angles are similar to its reported analogues [5–12].

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