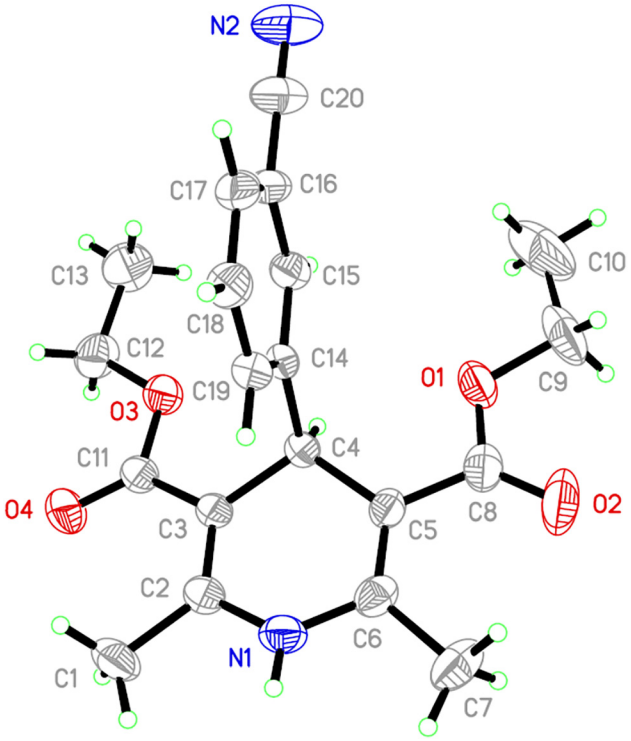
Zhang Li*, Yu Hai-yan, Wang Ying-lei, Sun Ke-nan and Tian Ye

The crystal structure of diethyl 1,4-dihydro-2,6-dimethyl-4-(3-cyanophenyl)-3,5-pyridinedicarboxylate, $C_{20}H_{22}N_2O_4$



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Abstract

$C_{20}H_{22}N_2O_4$, monoclinic, $P2_1/n$ (no. 14), a = 11.4033(15) Å, b = 14.2998(16) Å, c = 11.6486(16) Å, β = 91.197(8)°, V = 1899.1(4) Å^3, Z = 4, $R_{gt}(F)$ = 0.0513, $wR_{ref}(F^2)$ = 0.1542, T = 296.2 K.

***Corresponding author: Zhang Li**, School of Biological and Chemical Engineering, Nanyang Institute of Technology, Nanyang, 473004, China, E-mail: nyistzl@163.com. https://orcid.org/0000-0003-1817-9056
Yu Hai-yan, Wang Ying-lei, Sun Ke-nan and Tian Ye, [1]School of Biological and Chemical Engineering, Nanyang Institute of Technology, Nanyang, 473004, China

Table 1: Data collection and handling.

Crystal:	Colorless block
Size:	0.26 × 0.21 × 0.15 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}:	9580, 3405, 0.052
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\sigma(I_{obs})$, 2047
$N(param)_{refined}$:	240
Programs:	Bruker [1], OLEX2 [2], SHELX [3, 4]

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Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

1 Source of materials

All reagents were commercial and used as received without any further purification. The title compound was synthesized using a one-pot protocol: 0.2 mmol ethyl acetoacetate, 0.10 mmol ammonium acetate, and 0.1 mmol 3-cyanobenzaldehyde was mixed in 50 mL anhydrous ethanol solution, then heated at 333 K for 5 h. After cooling, the precipitate was collected and recrystallized from 95 % ethanol, yield 56.3 % (based on 3-cyanobenzaldehyde). Colorless block crystals were obtained from the filtrate of recrystallization.

2 Experimental details

The structure was solved by Direct Methods with the SHELXS-2018 program. All H-atoms from C and 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 = 0.860 Å.

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

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
C1	0.42337 (18)	0.67363 (13)	0.20947 (17)	0.0571 (5)
C2	0.53357 (17)	0.67827 (12)	0.17303 (15)	0.0482 (5)
C3	0.60857 (16)	0.59142 (10)	0.16449 (16)	0.0469 (5)
H3	0.652794	0.595619	0.093436	0.056*
C4	0.53317 (18)	0.50443 (12)	0.15751 (15)	0.0513 (5)
C5	0.42096 (19)	0.50544 (13)	0.19077 (16)	0.0589 (5)
C6	0.3375 (2)	0.42465 (15)	0.1919 (2)	0.0865 (8)
H6A	0.264622	0.444282	0.223882	0.130*
H6B	0.370539	0.375013	0.237658	0.130*
H6C	0.323858	0.402837	0.114811	0.130*
C7	0.34277 (19)	0.75352 (15)	0.2344 (2)	0.0783 (7)
H7A	0.311318	0.778198	0.163567	0.118*
H7B	0.385568	0.801629	0.274646	0.118*
H7C	0.279789	0.731926	0.280960	0.118*
C8	0.5871 (2)	0.41743 (14)	0.12024 (18)	0.0679 (6)
C9	0.7646 (3)	0.34807 (18)	0.0624 (3)	0.1119 (11)
H9A	0.728892	0.317322	−0.003850	0.134*
H9B	0.765273	0.304582	0.126297	0.134*
C10	0.8837 (3)	0.3768 (3)	0.0370 (4)	0.1564 (16)
H10A	0.881645	0.423175	−0.022608	0.235*
H10B	0.927664	0.323579	0.012022	0.235*
H10C	0.920321	0.402627	0.104843	0.235*
C11	0.58750 (18)	0.76813 (13)	0.14701 (17)	0.0559 (5)
C12	0.7608 (2)	0.84287 (14)	0.0883 (2)	0.0788 (7)
H12A	0.753299	0.887206	0.150768	0.095*
H12B	0.728878	0.871162	0.018715	0.095*
C13	0.8849 (2)	0.81820 (19)	0.0733 (3)	0.1043 (10)
H13A	0.890839	0.771981	0.013964	0.157*
H13B	0.916677	0.793520	0.144004	0.157*
H13C	0.927971	0.873019	0.052228	0.157*
C14	0.69650 (16)	0.58749 (10)	0.26462 (15)	0.0439 (5)
C15	0.81474 (18)	0.58795 (11)	0.24725 (17)	0.0535 (5)
H15	0.842494	0.589096	0.172751	0.064*
C16	0.89373 (18)	0.58671 (13)	0.33932 (19)	0.0593 (6)
C17	0.8544 (2)	0.58465 (12)	0.44981 (19)	0.0631 (6)
H17	0.907169	0.583909	0.511777	0.076*
C18	0.7365 (2)	0.58369 (13)	0.46704 (18)	0.0629 (6)
H18	0.708774	0.581974	0.541527	0.075*
C19	0.65818 (18)	0.58524 (11)	0.37599 (17)	0.0522 (5)
H19	0.578120	0.584757	0.389654	0.063*
C20	1.0166 (2)	0.58638 (17)	0.3184 (2)	0.0817 (7)
N1	0.37181 (15)	0.58773 (11)	0.22513 (16)	0.0660 (5)
H1	0.305174	0.585691	0.258275	0.079*
N2	1.1148 (2)	0.58546 (18)	0.3005 (2)	0.1146 (9)
O1	0.69910 (16)	0.43057 (9)	0.09091 (13)	0.0764 (5)
O3	0.69828 (12)	0.75780 (8)	0.11379 (12)	0.0640 (4)
O4	0.54187 (14)	0.84406 (9)	0.15300 (15)	0.0813 (5)
O00B	0.54265 (19)	0.34153 (11)	0.11552 (18)	0.1121 (7)

3 Comment

The 1,4-dihydropyridines, such as dimethyl or diethyl 4-phenyl-2,6-dimethyl-1,4-dihydro-pyridine-3,5-dicarboxyl-ate and its derivatives, have been synthesized because of their biological and pharmacologic activities [5, 6]. Some cyano-substituted crystal structures have been reported, including diethyl 4-(4-cyanophenyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate [7, 8], isobutyl methyl 1,4-dihydro-2,6-dimethyl-4-(3-cyanophenyl)-3,5-pyridinedicarboxylate [9], 2,6-dimethyl-3,5-bis(methoxycarbonyl)-4-(3-cyanophenyl)-1,4-dihydropyridine [10].

The title compound crystallizes in the monoclinic space group, $P2_1/n$. The conformational details and atom numbering of the title compound are shown in the figure. The asymmetric unit is made of one title molecule (see the figure). The 1,4-dihydropyridine ring adopts a flat-boat conformation, when the two ethoxycarbonyl groups are twisted in opposite directions. The plane of the 3-cyanophenyl group is approximately perpendicular to the 1,4-dihydropyridine ring. An infinite supramolecular chain is generated by intermolecular hydrogen bond N1–H1A···N2 with the distance of D···A 3.077 Å and the angle of D–H···A 165.90°. All bond lengths and angles are comparable with its reported analogues [11–13].

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Conflict of interest statement: The authors declare no conflicts of interest regarding this article.

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