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Ethyl 6-amino-5-cyano-2-methyl-4-propyl-4*H*-pyran-3-carboxylate

Qun-Di Yu,[a] Ke-Xin Li[b]* and Yun-Yu Liu[c]

[a]Food Science and Pharmacy College, Zhejiang Ocean University, Zhoushan 316000, People's Republic of China, [b]People's Hospital of Jilin Province, Changchun 130021, People's Republic of China, and [c]Department of Chemistry, Northeast Normal University, Changchun 130024, People's Republic of China
Correspondence e-mail: yunyuliu888@yahoo.com.cn

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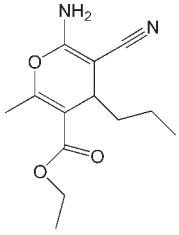
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.003 Å; R factor = 0.046; wR factor = 0.129; data-to-parameter ratio = 16.4.

The pyran ring of the title compound, $C_{13}H_{18}N_2O_3$, is almost planar (r.m.s. deviation = 0.059 Å). The crystal packing is stabilized by N—H···O and N—H···N hydrogen bonds.

Related literature

Ethyl 6-amino-5-cyano-2-methyl-4-propyl-4*H*-pyran-3-carboxylate and its derivatives are widely utilized as organic intermediates, see: Liang *et al.* (2009).



Experimental

Crystal data

$C_{13}H_{18}N_2O_3$
M_r = 250.15
Triclinic, $P\overline{1}$
a = 8.1172 (9) Å
b = 8.7956 (9) Å
c = 11.2877 (19) Å
α = 106.082 (12)°
β = 107.274 (12)°
γ = 103.315 (9)°
V = 695.20 (19) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.09 mm^{-1}
T = 293 K
0.25 × 0.23 × 0.20 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 1998)
T_{min} = 0.65, T_{max} = 0.87
5049 measured reflections
2826 independent reflections
1577 reflections with $I > 2\sigma(I)$
R_{int} = 0.023

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.046
$wR(F^2)$ = 0.129
S = 0.89
2826 reflections
172 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.13 e Å^{-3}
$\Delta\rho_{min}$ = −0.22 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2A···O1^{i}	0.805 (18)	2.088 (19)	2.881 (2)	168.2 (17)
N2—H2B···N1^{ii}	0.85 (2)	2.21 (2)	3.035 (3)	164.4 (17)

Symmetry codes: (i) $x-1, y, z$; (ii) $-x-1, -y-1, -z+1$.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1998); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BT5109).

References

Bruker (1998). *SMART*, *SAINT* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
Liang, F., Cheng, X., Liu, J. & Liu, Q. (2009). *Chem. Commun.* pp. 3636–3538.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

supporting information

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S1. Comment

Ethyl 6-amino-5-cyano-2-methyl-4-propyl-4H-pyran-3-carboxylate and its derivatives are widely utilized as organic intermediates (Liang *et al.*, 2009).

The pyran ring of the title compound, $C_{13}H_{18}N_2O_3$, is almost planar (r.m.s. deviation 0.059Å). The crystal packing is stabilized by N-H···O and N-H···N hydrogen bonds.

S2. Experimental

A mixture of butyraldehyde (1.0 mmol), malononitrile (1.0 mmol) and acetyl acetate (1.0 mmol) was dissolved in 5 mL dimethylformamide and catalytic amount of piperidine (0.2 mmol) was added at room temperature under stirring. After 2h, the reaction mixture was poured into water and extracted with CH_2Cl_2. The combined organic phase was washed with water, dried over $MgSO_4$, filtered and concentrated in vacuo. The crude product was purified by silica column chromatography. Yield: 87%. Pure product was dissolved in a mixture of petroleum ether. The single-crystals were obtained by slow evaporation of the solvents.

S3. Refinement

All H atoms on C atoms were positioned geometrically (C—H = 0.93-0.98Å) and refined as riding, with U_{iso}(H)=1.2U_{eq}(C) or U_{iso}(H)=1.5U_{eq}(C_{methyl}). The H atoms bonded to N were freely refined.

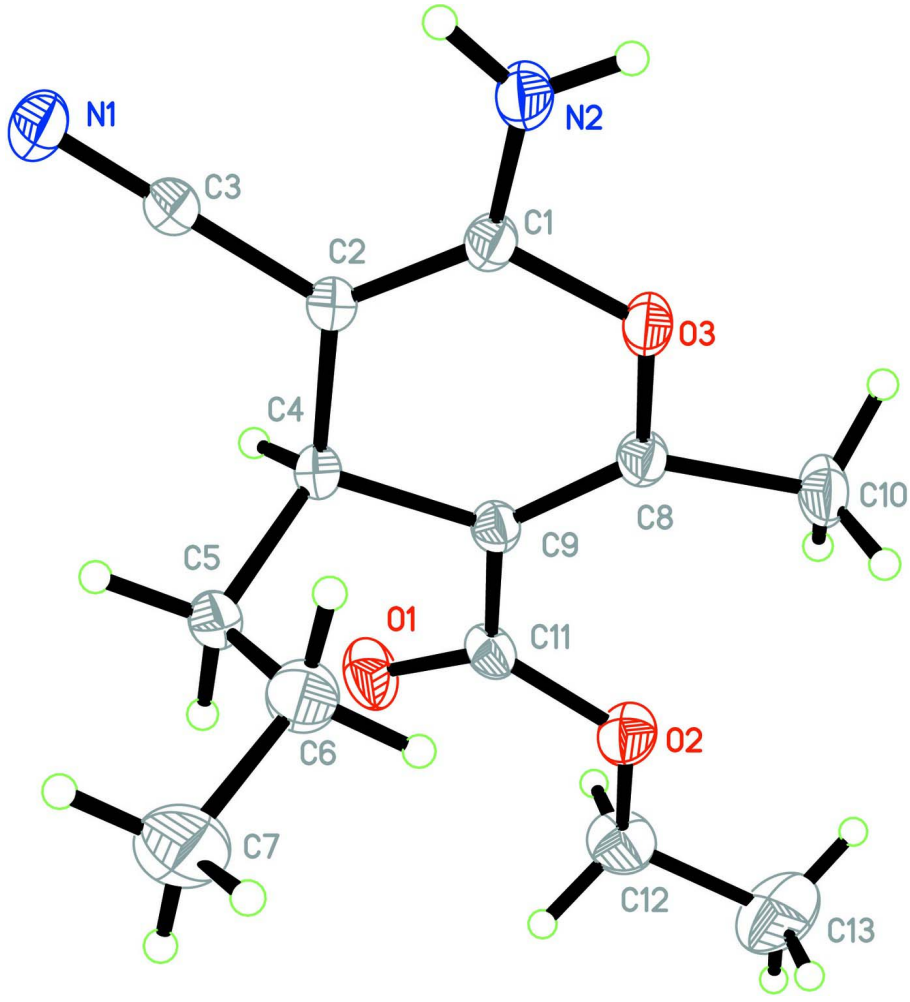

Figure 1

The structure of the title compound, showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

Ethyl 6-amino-5-cyano-2-methyl-4-propyl-4*H*-pyran-3-carboxylate

Crystal data

$C_{13}H_{18}N_2O_3$
$M_r = 250.15$
Triclinic, $P\overline{1}$
Hall symbol: -P 1
$a = 8.1172\ (9)$ Å
$b = 8.7956\ (9)$ Å
$c = 11.2877\ (19)$ Å
$\alpha = 106.082\ (12)°$
$\beta = 107.274\ (12)°$
$\gamma = 103.315\ (9)°$
$V = 695.20\ (19)$ Å^3

$Z = 2$
$F(000) = 268$
$D_x = 1.195$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 2826 reflections
$\theta = 3.0–26.4°$
$\mu = 0.09$ mm^{-1}
$T = 293$ K
Block, colorless
0.25 × 0.23 × 0.20 mm

Data collection

Bruker APEX CCD area-detector diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 1998)
T_{min} = 0.65, T_{max} = 0.87
5049 measured reflections
2826 independent reflections
1577 reflections with $I > 2\sigma(I)$
R_{int} = 0.023
θ_{max} = 26.4°, θ_{min} = 2.6°
h = −10→10
k = −10→10
l = −13→14

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.046
$wR(F^2)$ = 0.129
S = 0.89
2826 reflections
172 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0757P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.13 e Å^{-3}
$\Delta\rho_{min}$ = −0.22 e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2$sigma(F^2) is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	−0.2429 (2)	−0.09571 (19)	0.63342 (17)	0.0444 (4)
C2	−0.1346 (2)	−0.18666 (19)	0.61071 (16)	0.0428 (4)
C3	−0.2165 (2)	−0.3640 (2)	0.55184 (18)	0.0507 (5)
C4	0.0703 (2)	−0.10825 (19)	0.65363 (16)	0.0416 (4)
H4	0.1012	−0.1530	0.5765	0.050*
C5	0.1778 (2)	−0.1557 (2)	0.76684 (17)	0.0513 (5)
H5A	0.1418	−0.2774	0.7362	0.062*
H5B	0.3075	−0.1117	0.7850	0.062*
C6	0.1500 (3)	−0.0922 (3)	0.8948 (2)	0.0716 (6)
H6A	0.0195	−0.1271	0.8756	0.086*
H6B	0.1976	0.0298	0.9305	0.086*
C7	0.2423 (4)	−0.1545 (3)	1.0004 (2)	0.1038 (9)
H7A	0.2186	−0.1102	1.0791	0.156*
H7B	0.3723	−0.1175	1.0223	0.156*
H7C	0.1945	−0.2753	0.9666	0.156*

C8	0.0021 (2)	0.1608 (2)	0.70345 (17)	0.0446 (4)
C9	0.1207 (2)	0.08115 (19)	0.69043 (16)	0.0404 (4)
C10	0.0223 (3)	0.3431 (2)	0.7354 (2)	0.0670 (6)
H10A	−0.0868	0.3524	0.6792	0.101*
H10B	0.1258	0.3989	0.7199	0.101*
H10C	0.0409	0.3947	0.8274	0.101*
C11	0.3091 (2)	0.1666 (2)	0.70545 (18)	0.0466 (4)
C12	0.5617 (3)	0.4184 (3)	0.7863 (2)	0.0737 (6)
H12A	0.5646	0.4016	0.6984	0.088*
H12B	0.6491	0.3749	0.8326	0.088*
C13	0.6091 (4)	0.5982 (3)	0.8618 (3)	0.1117 (9)
H13A	0.7300	0.6584	0.8713	0.168*
H13B	0.6061	0.6135	0.9486	0.168*
H13C	0.5222	0.6403	0.8149	0.168*
N2	−0.4192 (2)	−0.1503 (2)	0.61418 (18)	0.0606 (5)
N1	−0.2822 (2)	−0.5075 (2)	0.50412 (19)	0.0763 (6)
O3	−0.17565 (15)	0.07590 (13)	0.68500 (12)	0.0530 (3)
O1	0.39733 (18)	0.09129 (16)	0.65942 (14)	0.0694 (4)
O2	0.37809 (16)	0.33123 (15)	0.77399 (14)	0.0612 (4)
H2A	−0.472 (2)	−0.083 (2)	0.6160 (17)	0.055 (5)*
H2B	−0.485 (3)	−0.253 (3)	0.585 (2)	0.062 (6)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0435 (10)	0.0357 (9)	0.0503 (11)	0.0118 (8)	0.0178 (8)	0.0123 (8)
C2	0.0427 (10)	0.0356 (9)	0.0466 (10)	0.0149 (8)	0.0133 (8)	0.0131 (8)
C3	0.0410 (10)	0.0451 (11)	0.0606 (12)	0.0174 (9)	0.0140 (9)	0.0157 (9)
C4	0.0439 (10)	0.0366 (9)	0.0449 (10)	0.0182 (8)	0.0168 (8)	0.0129 (7)
C5	0.0490 (11)	0.0426 (10)	0.0593 (12)	0.0179 (8)	0.0138 (9)	0.0205 (9)
C6	0.0846 (16)	0.0705 (14)	0.0584 (13)	0.0299 (12)	0.0213 (11)	0.0261 (11)
C7	0.130 (2)	0.109 (2)	0.0662 (15)	0.0379 (18)	0.0184 (15)	0.0482 (16)
C8	0.0421 (10)	0.0380 (9)	0.0533 (11)	0.0135 (8)	0.0195 (8)	0.0152 (8)
C9	0.0412 (10)	0.0380 (9)	0.0441 (10)	0.0155 (8)	0.0161 (8)	0.0173 (8)
C10	0.0593 (13)	0.0393 (10)	0.1052 (17)	0.0212 (9)	0.0362 (12)	0.0222 (11)
C11	0.0453 (10)	0.0486 (11)	0.0552 (11)	0.0215 (9)	0.0197 (9)	0.0281 (9)
C12	0.0484 (12)	0.0710 (14)	0.0989 (17)	0.0079 (11)	0.0285 (12)	0.0374 (13)
C13	0.0887 (19)	0.0724 (17)	0.134 (3)	−0.0179 (14)	0.0439 (18)	0.0169 (17)
N2	0.0453 (10)	0.0414 (10)	0.0917 (13)	0.0153 (9)	0.0289 (9)	0.0167 (9)
N1	0.0583 (11)	0.0403 (10)	0.1089 (15)	0.0124 (9)	0.0212 (10)	0.0126 (10)
O3	0.0443 (7)	0.0348 (6)	0.0765 (9)	0.0148 (6)	0.0265 (6)	0.0115 (6)
O1	0.0578 (9)	0.0646 (9)	0.1057 (12)	0.0336 (7)	0.0447 (8)	0.0355 (8)
O2	0.0470 (7)	0.0474 (8)	0.0829 (10)	0.0073 (6)	0.0285 (7)	0.0184 (7)

Geometric parameters (Å, º)

C1—N2	1.329 (2)	C8—C9	1.333 (2)
C1—C2	1.350 (2)	C8—O3	1.3862 (19)

C1—O3	1.3638 (19)	C8—C10	1.501 (2)
C2—C3	1.415 (2)	C9—C11	1.476 (2)
C2—C4	1.512 (2)	C10—H10A	0.9600
C3—N1	1.145 (2)	C10—H10B	0.9600
C4—C9	1.522 (2)	C10—H10C	0.9600
C4—C5	1.540 (2)	C11—O1	1.2122 (18)
C4—H4	0.9800	C11—O2	1.326 (2)
C5—C6	1.502 (3)	C12—O2	1.456 (2)
C5—H5A	0.9700	C12—C13	1.467 (3)
C5—H5B	0.9700	C12—H12A	0.9700
C6—C7	1.517 (3)	C12—H12B	0.9700
C6—H6A	0.9700	C13—H13A	0.9600
C6—H6B	0.9700	C13—H13B	0.9600
C7—H7A	0.9600	C13—H13C	0.9600
C7—H7B	0.9600	N2—H2A	0.805 (18)
C7—H7C	0.9600	N2—H2B	0.85 (2)

N2—C1—C2	128.59 (16)	C9—C8—C10	130.81 (16)
N2—C1—O3	110.12 (13)	O3—C8—C10	107.27 (12)
C2—C1—O3	121.28 (15)	C8—C9—C11	123.41 (14)
C1—C2—C3	117.85 (15)	C8—C9—C4	122.47 (15)
C1—C2—C4	122.94 (14)	C11—C9—C4	114.08 (12)
C3—C2—C4	119.09 (12)	C8—C10—H10A	109.5
N1—C3—C2	179.8 (2)	C8—C10—H10B	109.5
C2—C4—C9	109.31 (11)	H10A—C10—H10B	109.5
C2—C4—C5	111.67 (13)	C8—C10—H10C	109.5
C9—C4—C5	112.78 (13)	H10A—C10—H10C	109.5
C2—C4—H4	107.6	H10B—C10—H10C	109.5
C9—C4—H4	107.6	O1—C11—O2	121.58 (16)
C5—C4—H4	107.6	O1—C11—C9	122.36 (16)
C6—C5—C4	114.61 (13)	O2—C11—C9	116.06 (13)
C6—C5—H5A	108.6	O2—C12—C13	107.97 (17)
C4—C5—H5A	108.6	O2—C12—H12A	110.1
C6—C5—H5B	108.6	C13—C12—H12A	110.1
C4—C5—H5B	108.6	O2—C12—H12B	110.1
H5A—C5—H5B	107.6	C13—C12—H12B	110.1
C5—C6—C7	113.67 (18)	H12A—C12—H12B	108.4
C5—C6—H6A	108.8	C12—C13—H13A	109.5
C7—C6—H6A	108.8	C12—C13—H13B	109.5
C5—C6—H6B	108.8	H13A—C13—H13B	109.5
C7—C6—H6B	108.8	C12—C13—H13C	109.5
H6A—C6—H6B	107.7	H13A—C13—H13C	109.5
C6—C7—H7A	109.5	H13B—C13—H13C	109.5
C6—C7—H7B	109.5	C1—N2—H2A	117.1 (13)
H7A—C7—H7B	109.5	C1—N2—H2B	124.7 (13)
C6—C7—H7C	109.5	H2A—N2—H2B	117.0 (18)
H7A—C7—H7C	109.5	C1—O3—C8	120.17 (11)
H7B—C7—H7C	109.5	C11—O2—C12	116.81 (13)

C9—C8—O3	121.91 (14)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2*A*···O1^{i}	0.805 (18)	2.088 (19)	2.881 (2)	168.2 (17)
N2—H2*B*···N1^{ii}	0.85 (2)	2.21 (2)	3.035 (3)	164.4 (17)

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