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

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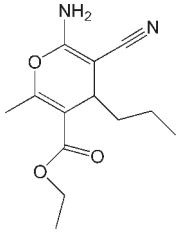
Key indicators: single-crystal X-ray study; $T$ = 293 K; mean $\sigma$(C–C) = 0.003 Å; $R$ factor = 0.046; $wR$ factor = 0.129; data-to-parameter ratio = 16.4.

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
$\alpha$ = 106.082 (12)°
$\beta$ = 107.274 (12)°
$\gamma$ = 103.315 (9)°
$V$ = 695.20 (19) Å$^3$
$Z$ = 2
Mo $K\alpha$ radiation
$\mu$ = 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—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) |

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.

# supplementary materials

*Acta Cryst.* (2009). E**65**, o2862 [ **doi:10.1107/S1600536809043748** ]

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

**Q.-D. Yu, K.-X. Li and Y.-Y. Liu**

## 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.

## 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.

## Refinement

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

## Figures

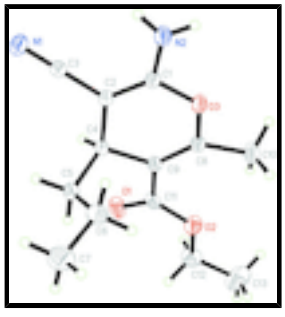

Fig. 1. The structure of the title compound, showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

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

*Crystal data*

$C_{13}H_{18}N_2O_3$ $Z = 2$

| | |
|---|---|
| $M_r$ = 250.15 | $F_{000}$ = 268 |
| Triclinic, $P\bar{1}$ | $D_x$ = 1.195 Mg m$^{-3}$ |
| Hall symbol: -P 1 | Mo $K\alpha$ radiation, λ = 0.71073 Å |
| $a$ = 8.1172 (9) Å | Cell parameters from 2826 reflections |
| $b$ = 8.7956 (9) Å | θ = 3.0–26.4º |
| $c$ = 11.2877 (19) Å | μ = 0.09 mm$^{-1}$ |
| α = 106.082 (12)º | $T$ = 293 K |
| β = 107.274 (12)º | Block, colorless |
| γ = 103.315 (9)º | 0.25 × 0.23 × 0.20 mm |
| $V$ = 695.20 (19) Å$^3$ | |

*Data collection*

| | |
|---|---|
| Bruker APEX CCD area-detector diffractometer | 2826 independent reflections |
| Radiation source: fine-focus sealed tube | 1577 reflections with $I > 2\sigma(I)$ |
| Monochromator: graphite | $R_{int}$ = 0.023 |
| $T$ = 293 K | $\theta_{max}$ = 26.4º |
| φ and ω scans | $\theta_{min}$ = 2.6º |
| Absorption correction: multi-scan (SADABS; Bruker, 1998) | $h$ = −10→10 |
| $T_{min}$ = 0.65, $T_{max}$ = 0.87 | $k$ = −10→10 |
| 5049 measured reflections | $l$ = −13→14 |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | Secondary atom site location: difference Fourier map |
| Least-squares matrix: full | Hydrogen site location: inferred from neighbouring sites |
| $R[F^2 > 2\sigma(F^2)]$ = 0.046 | H atoms treated by a mixture of independent and constrained refinement |
| $wR(F^2)$ = 0.129 | $w = 1/[\sigma^2(F_o^2) + (0.0757P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$ |
| $S$ = 0.89 | $(\Delta/\sigma)_{max} < 0.001$ |
| 2826 reflections | $\Delta\rho_{max}$ = 0.13 e Å$^{-3}$ |
| 172 parameters | $\Delta\rho_{min}$ = −0.21 e Å$^{-3}$ |
| Primary atom site location: structure-invariant direct methods | Extinction correction: none |

*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 $F^2 > 2\text{sigma}(F^2)$ is used only for calculat-

ing 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 (Å$^2$)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| 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, °)*

| | | | |
|---|---|---|---|
| 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, °)*

| *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.

**Fig. 1**