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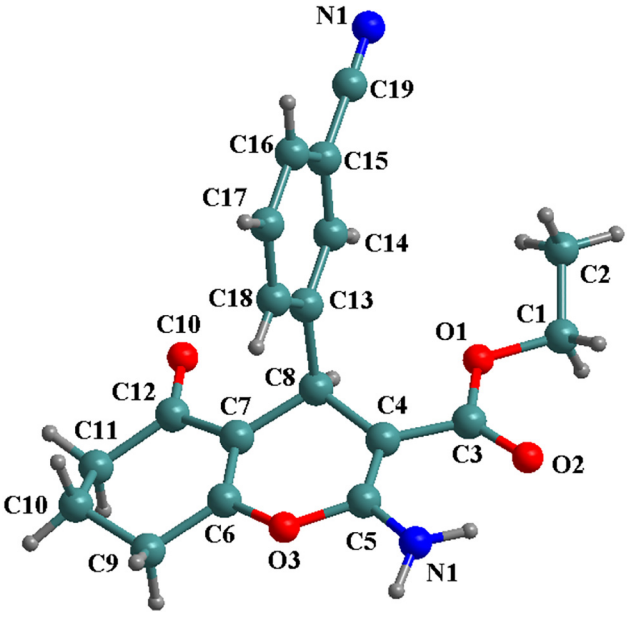
The crystal structure of ethyl 2-amino-4-(cyanophenyl)-5-oxo-5,6,7,8-tetrahydro-4*H*-chromene-3-carboxylate, $C_{19}H_{18}N_2O_4$



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Abstract

$C_{19}H_{18}N_2O_4$, triclinic, *P*21/*n* (no. 14), *a* = 11.930(6) Å, *b* = 7.638(4) Å, *c* = 18.370(4) Å, *β* = 97.959(9)°, *V* = 1657.9(13) Å^3, *Z* = 4, $R_{gt}(F)$ = 0.0497, $wR_{ref}(F^2)$ = 0.1437, *T* = 296(2) K.

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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

The title compound, ethyl 2-amino-4-(cyanophenyl)-5-oxo-5,6,7,8-tetrahydro-4*H*-chromene-3-carboxylate, was obtained by a three-component reaction using 4-(dimethylamino) pyridine (DMAP) as the catalyst. A 50 mL ethanol solution of 3-cyanobenzaldehyde (10 mmol), ethyl 2-cyanoacetate (10 mmol), and cyclohexane-1,3-dione (10 mmol), DMAP (1 mmol) was heated at 353 K for 5 h. The solid was filtered and recrystallized from an ethanol solution to give crystals of the title compound, yield 67.6 % (based on 3-cyanobenzaldehyde). Colorless block crystals were obtained by recrystallization.

Table 1: Data collection and handling.

Crystal:	Colorless block
Size:	0.29 × 0.24 × 0.21 mm
Wavelength:	Mo *K*α radiation (0.71073 Å)
μ:	0.10 mm^{-1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
θ_{max}, completeness:	28.5°, >99 %
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	10,157, 4,085, 0.032
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\sigma(I_{obs})$, 2,841
$N(\text{param})_{refined}$:	236
Programs:	Bruker[1], Olex2[2], SHELX[3,4]

2 Experimental details

The structure was solved by Direct Methods with the SHELXL-2014 program. All H-atoms from C 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, 0.970 and 0.980 Å, and N–H = 0.861 and 0.861 Å, respectively.

3 Comment

Known as pharmacological activities, 2-amino-4*H*-pyran-3-carboxylate derivatives, such as ethyl 2-amino-4-(4-ethoxyphenyl)-5-oxo-5,6,7,8-tetrahydro-4*H*-1-benzopyran-3-carboxylate[5] and ethyl 2-amino-4-(phenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4*H*-1-benzopyran-3-carboxylate and their derivatives,[6–14] have been synthesized through a famous three-component reaction and their single crystal structures have been

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

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
C1	0.75682 (15)	−0.0751 (3)	0.72892 (11)	0.0583 (5)
H1A	0.753771	−0.201511	0.733417	0.070*
H1B	0.788970	−0.027157	0.776109	0.070*
C2	0.82699 (16)	−0.0272 (3)	0.67285 (11)	0.0670 (6)
H2A	0.792347	−0.069317	0.625826	0.100*
H2B	0.900648	−0.078764	0.684708	0.100*
H2C	0.834075	0.097841	0.671187	0.100*
C3	0.58202 (14)	0.0259 (2)	0.76101 (9)	0.0411 (4)
C4	0.47111 (13)	0.0913 (2)	0.73216 (8)	0.0364 (3)
C5	0.39825 (14)	0.1307 (2)	0.77968 (8)	0.0410 (4)
C6	0.24591 (13)	0.1521 (2)	0.68371 (8)	0.0396 (4)
C7	0.31258 (12)	0.12308 (19)	0.63290 (8)	0.0353 (3)
C8	0.43931 (12)	0.12062 (19)	0.65055 (8)	0.0332 (3)
H8	0.467778	0.021457	0.624643	0.040*
C9	0.12076 (14)	0.1603 (3)	0.67099 (10)	0.0513 (4)
H9A	0.094995	0.253877	0.700294	0.062*
H9B	0.089839	0.051048	0.686343	0.062*
C10	0.07861 (15)	0.1922 (3)	0.59106 (11)	0.0631 (5)
H10A	−0.002223	0.170307	0.582231	0.076*
H10B	0.090896	0.314071	0.579679	0.076*
C11	0.13535 (15)	0.0801 (3)	0.54124 (11)	0.0618 (5)
H11A	0.111713	0.116575	0.490881	0.074*
H11B	0.111167	−0.040157	0.545893	0.074*
C12	0.26206 (13)	0.0881 (2)	0.55709 (9)	0.0420 (4)
C13	0.49243 (11)	0.28690 (19)	0.62538 (7)	0.0322 (3)
C14	0.57863 (12)	0.2782 (2)	0.58289 (8)	0.0383 (4)
H14	0.602990	0.170158	0.567810	0.046*
C15	0.62905 (13)	0.4305 (2)	0.56262 (8)	0.0455 (4)
C16	0.59375 (16)	0.5921 (2)	0.58354 (9)	0.0521 (5)
H16	0.627905	0.693882	0.569587	0.062*
C17	0.50723 (16)	0.6001 (2)	0.62537 (10)	0.0512 (4)
H17	0.482213	0.708271	0.639887	0.061*
C18	0.45719 (13)	0.4493 (2)	0.64599 (9)	0.0406 (4)
H18	0.398553	0.456894	0.674343	0.049*
C19	0.71870 (16)	0.4175 (3)	0.51764 (10)	0.0605 (5)
N1	0.41997 (17)	0.1357 (2)	0.85303 (8)	0.0561 (4)
H1C	0.359 (2)	0.140 (3)	0.8794 (12)	0.071 (6)*
H1D	0.490 (2)	0.097 (3)	0.8713 (13)	0.079 (7)*
N2	0.78706 (18)	0.4054 (3)	0.48128 (11)	0.0896 (7)
O1	0.64441 (9)	−0.00630 (16)	0.70772 (6)	0.0448 (3)
O2	0.61719 (11)	0.0012 (2)	0.82548 (7)	0.0634 (4)
O3	0.28786 (9)	0.17702 (16)	0.75678 (6)	0.0478 (3)
O4	0.32137 (10)	0.06027 (18)	0.50958 (6)	0.0543 (3)

also reported. The title compound crystallizes in monoclinic system, $P2_1/n$ group (no. 14) with the fomula of $C_{19}H_{18}N_2O_4$. Whereas the 3-cyanophenyl group is almost coplanar, the 4-hydropyran ring is slightly twisted from planarity.[14] The 1D chains are generated through the hydrogen bonds N1–H1A···N2, which are linked to form a 3D supramolecular structure by complicated hydrogen bonds C14–H14···O4, C16–H16···O4, and C2–H2A···O4. All the bond lengths and angles are similar to the reported results.[5–14]

Author contribution: All the authors have accepted responsibility for the entire content of this submitted manuscript and approved submission.

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

References

1. Bruker. SAINT v7.60A; Bruker AXS Inc: Madison, Wisconsin, USA, 2009.
2. Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. OLEX2: A Complete Structure Solution, Refinement and Analysis Program. *J. Appl. Crystallogr.* **2009**, *42*, 339–341.
3. Sheldrick, G. M. Crystal Structure Refinement with SHELXL. *Acta Crystallogr.* **2015**, *C71*, 3–8.
4. Sheldrick, G. Using Phases to Determine the Space Group. *Acta Crystallogr.* **2018**, *A74*, A353.
5. Chen, H.; Yang, G.; Liao, X.; Bao, Z.; Zhan, X. Crystal Structure and Anti-Lung Cancer Activity of Novel Pyran Derivatives from Traditional Chinese Medicine. *Lat. Am. J. Pharm.* **2018**, *37*, 359–362.
6. Shi, D.; Zhang, S.; Wang, X.; Zhuang, Q. Ethyl 2-Amino-4-(4-Fluorophenyl)-7,7-Dimethyl 5-Oxo-5,6,7,8-Tetrahydro-4*H*-Benzo[*b*] pyran-3-carboxylate. *Acta Crystallogr.* **2003**, *E59*, o1501–o1502.
7. Khan, A. T.; Lal, M.; Ali, S.; Khan, M. M. One-Pot Three Component Reaction for the Synthesis of Pyran Annulated Heterocyclic Compounds Using DMAP as a Catalyst. *Tetrahedron Lett.* **2011**, *52*, 5327–5332.
8. Xiao, Y.-S.; Zhang, L.; Hu, W.-L.; Zhao, Y.-B.; Hu, H. In Vitro Activity of Synthesized Pyran Derivatives-Inhibitor Against Prostate Cancer. *Lat. Am. J. Pharm.* **2017**, *36*, 609–612.
9. Nongrum, R.; Nongthombam, G. R.; Kharkongor, M.; Rani, J. W. S.; Rahman, N.; Kathing, C.; Myrboh, B.; Nongkhlaw, R. A Nano-Organo Catalyzed Route towards the Efficient Synthesis of Benzo[*b*]pyran Derivatives Under Ultrasonic Irradiation. *RSC Adv.* **2016**, *6*, 108384–108392.
10. Yang, D.-Q.; Li, Z.-M. Crystal Structure of Ethyl 2-Amino-4-(3-Cyanophenyl)-7,7-Dimethyl-5-Oxo-5,6,7,8-Tetrahydro-4*H*-Chromene-3-Carboxylate, $C_{21}H_{22}N_2O_4$. *Z. Kristallogr. N. Cryst. Struct.* **2018**, *233*, 903–904.
11. Ramireddy, N.; Abbaraju, S.; Ding, D.; Arman, H.; Zhao, J. C.-G. Organocatalyzed Enantioselective Synthesis of 2-Amino-4*H*-Chromene Derivatives. *J. Heterocycl. Chem.* **2017**, *54*, 677–691.
12. Shin, S. Y.; Yoo, M.; Koh, D. The Crystal Structure of Ethyl 2-Amino-4-(3,5-Difluorophenyl)-7,7-Dimethyl-5-Oxo-5,6,7,8-Tetrahydro-4*H*-Chromene-3-Carboxylate, $C_{20}H_{21}F_2NO_4$. *Z. Kristallogr. N. Cryst. Struct.* **2021**, *236*, 307–309.
13. Wang, X.-S.; Shi, D.-Q.; Tu, S.-J.; Yao, C.-S. A Convenient Synthesis of 5-Oxo-5,6,7,8-Tetrahydro-4*H*-Benzo-[*b*]-Pyran Derivatives Catalyzed by KF–Alumina. *Synth. Commun.* **2003**, *33*, 119–126.
14. Fan, X.-X.; Shen, P.; Zhou, X.-H.; Khrustalev, V. N.; Rivera, D. G.; Nenajdenko, V. G. Three-Component Synthesis and Crystal Structure of 2-Amino-3-Cyano-4*H*-Pyran and -Thiopyran Derivatives. *Russ. J. Org. Chem.* **2022**, *58*, 1786–1796.