

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

Yuling Li,^a Xiangshan Wang,^{a*}
Zhaosen Zeng,^a Daqing Shi,^a
Xianyong Wei^b and
Zhimin Zong^b^aDepartment of Chemistry, Xuzhou Normal University, Xuzhou 221116, People's Republic of China, and ^bSchool of Chemical Engineering, China University of Mining and Technology, Xuzhou 221008, People's Republic of ChinaCorrespondence e-mail:
xswang1974@yahoo.com

Key indicators

Single-crystal X-ray study
 $T = 289$ K
Mean $\sigma(\text{C}-\text{C}) = 0.003$ Å
Disorder in main residue
 R factor = 0.044
 wR factor = 0.110
Data-to-parameter ratio = 11.9For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The title compound, $\text{C}_{16}\text{H}_{16}\text{N}_2\text{O}_3$, was synthesized by the reaction of phenylmethylidenemalononitrile and ethyl acetate in the presence of triethylbenzylammonium chloride in an aqueous medium. The pyran ring adopts a boat conformation. The phenyl ring and the basal plane of the pyran ring make a dihedral angle of $94.5(2)^\circ$. Intermolecular $\text{N}-\text{H}\cdots\text{O}$ and $\text{N}-\text{H}\cdots\text{N}$ hydrogen bonds link the molecules into ribbons along the a axis.

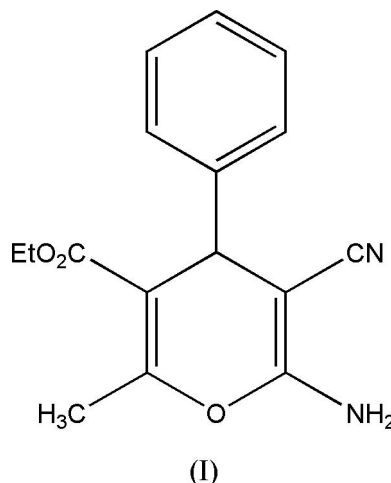
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Comment

2-Aminopyran derivatives are often used in cosmetics and pigments, and utilized as potentially biodegradable agrochemicals (Morinaka & Takahashi, 1977; Witte *et al.*, 1986; Hafez *et al.*, 1987). There are various methods of synthesizing 2-aminopyran derivatives, the most promising one using water as a reaction medium. It is known (Breslow & Rideout, 1980) that hydrophobic effects can seriously enhance the rate of organic reactions. We report here the crystal structure of the title compound, (I), synthesized in an aqueous medium.



In (I), the pyran ring is slightly distorted and adopts a boat conformation (Fig. 1). Atoms C3 and O1 deviate from the basal plane defined by the atoms C1/C2/C4/C5 by 0.236 (2) and 0.120 (2) Å, respectively. Similar distortion was observed in the structure of ethyl (2-amino-4-(3-nitrophenyl)-1,4-dihydro-2H-pyrano-[3,2-*h*]quinolin-3-yl)carboxylate (Wang *et al.*, 2004) and the structure of 9-(2-hydroxy-4,4-dimethyl-6-oxocyclohex-1-enyl)-3,3,7-trimethyl-1,2,3,4-hexahydro-7H-xanthenone (Li *et al.*, 2004). The basal plane of the pyran ring is nearly perpendicular to the phenyl ring C6–C11, making a dihedral angle of $94.5(2)^\circ$. All bond lengths and angles (Table 1) are normal.

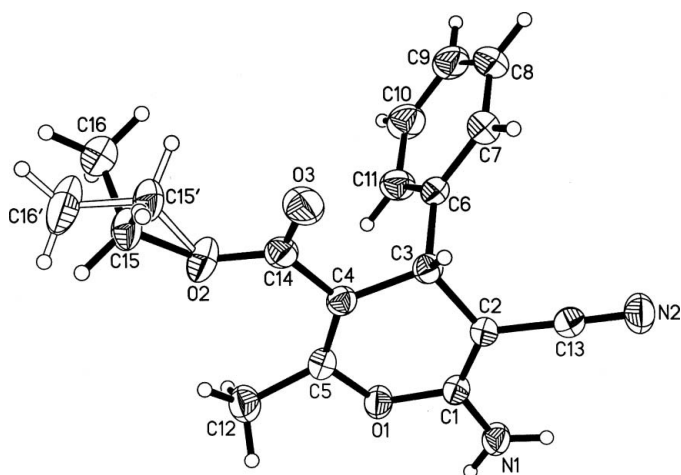


Figure 1
View of (I), showing the atom-numbering scheme, disorder of the ethyl group and 30% probability displacement ellipsoids.

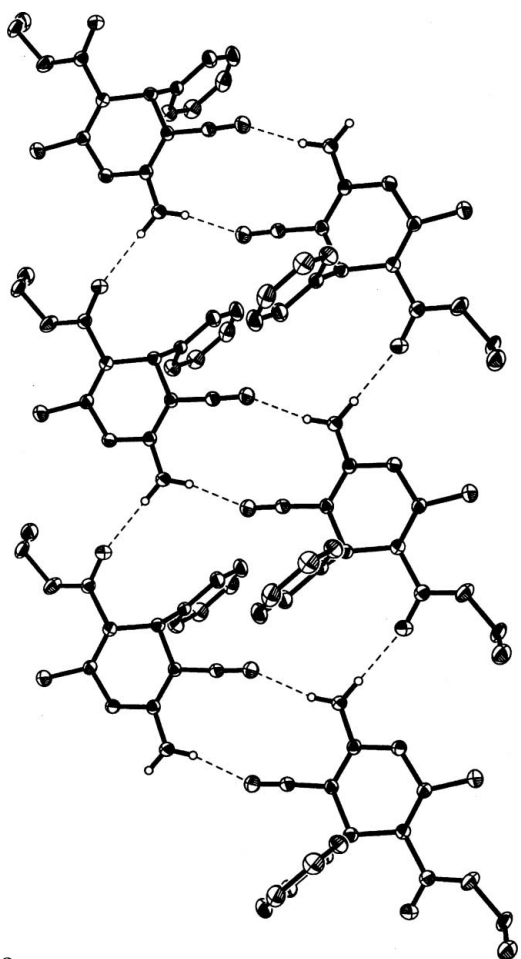


Figure 2
The hydrogen-bonded (dashed lines) ribbon in (I). Only one disorder component is shown.

Intermolecular N—H...O and N—H...N hydrogen bonds (Table 2), formed by the amino, cyano and carbonyl groups, link the molecules into the ribbons along the *a* axis (Fig. 2). The crystal packing (Fig. 3) is further stabilized by van der Waals forces.

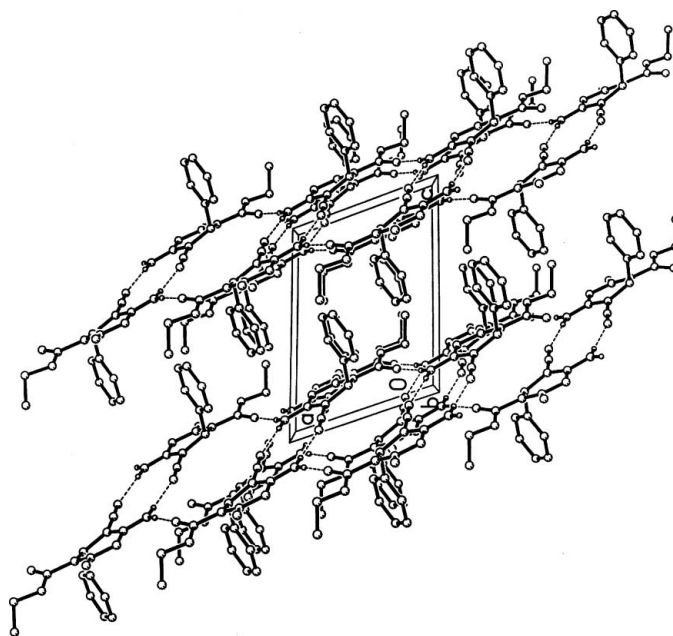


Figure 3
A molecular packing diagram of (I). Hydrogen bonds are shown as dashed lines. C-bound H atoms have been omitted.

Experimental

The title compound, (I), was prepared by the reaction of phenylmethylidenemalononitrile (0.31 g, 2 mmol) and ethyl acetoacetate (0.39 g, 3 mmol) in the presence of triethylbenzylammonium chloride (0.1 g) in water (10 ml) at 363 K for 8 h (yield 78%, mp. 465–467 K). Crystals of (I) suitable for X-ray diffraction were obtained by slow evaporation of an *N,N*-dimethylformamide solution.

Crystal data

$C_{16}H_{16}N_2O_3$	$Z = 2$
$M_r = 284.31$	$D_x = 1.282 \text{ Mg m}^{-3}$
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 8.1402 (16) \text{ \AA}$	Cell parameters from 28 reflections
$b = 9.3393 (19) \text{ \AA}$	$\theta = 3.5\text{--}27.7^\circ$
$c = 11.206 (2) \text{ \AA}$	$\mu = 0.09 \text{ mm}^{-1}$
$\alpha = 107.047 (3)^\circ$	$T = 289 (2) \text{ K}$
$\beta = 103.066 (4)^\circ$	Block, colorless
$\gamma = 106.257 (3)^\circ$	$0.44 \times 0.24 \times 0.18 \text{ mm}$
$V = 736.5 (2) \text{ \AA}^3$	

Data collection

Bruker <i>P4</i> diffractometer	$\theta_{\text{max}} = 25.0^\circ$
ω scans	$h = -9 \rightarrow 9$
Absorption correction: none	$k = -11 \rightarrow 10$
3837 measured reflections	$l = -7 \rightarrow 13$
2555 independent reflections	3 standard reflections
1859 reflections with $I > 2\sigma(I)$	every 97 reflections
$R_{\text{int}} = 0.035$	intensity decay: 2.8%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.056P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.044$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.110$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 0.97$	$\Delta\rho_{\text{max}} = 0.15 \text{ e \AA}^{-3}$
2555 reflections	$\Delta\rho_{\text{min}} = -0.15 \text{ e \AA}^{-3}$
215 parameters	Extinction correction: <i>SHELXL97</i>
H-atom parameters constrained	Extinction coefficient: 0.009 (3)

Table 1

Selected geometric parameters (Å, °).

O1—C1	1.3612 (18)	N1—C1	1.335 (2)
O1—C5	1.3915 (18)	C1—C2	1.352 (2)
O2—C14	1.321 (2)	C2—C3	1.513 (2)
O2—C15	1.474 (3)	C3—C4	1.508 (2)
O2—C15'	1.475 (3)	C4—C5	1.328 (2)
O3—C14	1.207 (2)		
C1—O1—C5	120.00 (13)	C4—C3—C2	109.47 (13)
C2—C1—O1	121.08 (14)	C5—C4—C3	122.26 (14)
C1—C2—C3	121.71 (14)	C4—C5—O1	121.34 (15)
C5—O1—C1—C2	−9.5 (2)	C2—C3—C4—C5	−16.3 (2)
O1—C1—C2—C3	−9.0 (2)	C3—C4—C5—O1	0.4 (2)
C1—C2—C3—C4	20.6 (2)	C1—O1—C5—C4	14.0 (2)

Table 2

Hydrogen-bonding geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N1—H1B...O3 ⁱ	0.87	2.08	2.949 (2)	176
N1—H1A...N2 ⁱⁱ	0.87	2.17	3.022 (2)	168

Symmetry codes: (i) $x - 1, y, z$; (ii) $-x, -y, 2 - z$.

The ethyl group shows a positional disorder over two sites (Fig. 1), with refined occupancies of 0.509 (6) and 0.491 (6). H atoms

were positioned geometrically and refined as riding, with C—H = 0.93–0.98, N—H = 0.87 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{parent atom})$.

Data collection: *XSCANS* (Siemens, 1994); cell refinement: *XSCANS*; data reduction: *SHELXTL* (Sheldrick, 1997); program(s) used to solve structure: *SHELXTL*; program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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