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Methyl 2-amino-4-(4-nitrophenyl)-5-oxo-5,6-dihydro-4*H*-pyrano[3,2-*c*]quinoline-3-carboxylate dimethylformamide solvate

Xiang-Shan Wang,[a,b]* Zhao-Sen Zeng,[b] Da-Qing Shi,[b] Hong Chen,[a] Xian-Yong Wei[a] and Zhi-Min Zong[a]

[a]School of Chemical Engineering, China University of Mining and Technology, Xuzhou 221008, People's Republic of China, and [b]Department of Chemistry, Xuzhou Normal University, Xuzhou 221116, People's Republic of China

Correspondence e-mail: xswang@xznu.edu.cn

Key indicators

Single-crystal X-ray study
T = 295 K
Mean σ(C–C) = 0.004 Å
Disorder in solvent or counterion
R factor = 0.065
wR factor = 0.209
Data-to-parameter ratio = 12.3

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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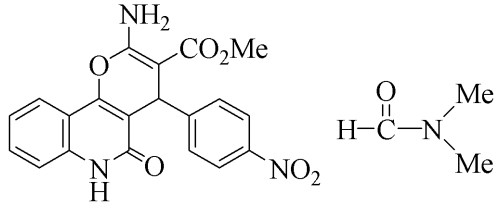
The title compound, $C_{20}H_{15}N_3O_6\cdot C_3H_7NO$, was synthesized by the reaction of methyl cyanoacetate, 4-nitrobenzaldehyde and 4-hydroxyquinolin-2-one in EtOH catalysed by KF-alumina, followed by crystallization from dimethylformamide. X-ray analysis reveals that the pyran ring adopts a boat conformation.

Comment

The synthesis of pyranoquinolines and their derivatives is of great interest in organic chemistry, because some of these compounds possess antibacterial activity (Madkour *et al.*, 2001) and moderate acetylcholine esterase inhibitory activity (Marco *et al.*, 2001), and act as antihypertensive agents (Jolivet *et al.*, 1996). The utility of fluoride salts as potential bases in a variety of synthetic reactions has been recognized in recent years. In particular, potassium fluoride coated with alumina (KF-alumina) has been a versatile solid-supported reagent used for many reactions (Clark, 1980) We report here the crystal structure of the title compound, (I).



(I)

In (I), the pyran ring of the pyranoquinoline moiety is slightly distorted and adopts a boat conformation (Fig. 1). Atoms C10 and O1 deviate from the basal plane defined by atoms C1, C9, C11 and C12 by 0.300 (2) and 0.176 (2) Å, respectively. Similar distortions were observed in ethyl 2-amino-4-(3-nitrophenyl)-1,4-dihydro-2*H*-pyrano[3,2-*h*]quinoline-3-carboxylate (Wang, Shi *et al.*, 2004), 9-(2-hydroxy-4,4-dimethyl-6-oxocyclohex-1-enyl)-3,3,7-trimethyl-1,2,3,4-hexahydro-9*H*-xanthene-1-one (Li *et al.*, 2004) and methyl 2-amino-4-(4-methylphenyl)-5-oxo-5,6-dihydro-4*H*-pyrano[3,2-*c*]quinoline-3-carboxylate dimethylformamide solvate (Wang, Zeng *et al.*, 2004). The basal plane of the pyran ring is nearly perpendicular to the C13–C18 benzene ring, forming a dihedral angle of 87.5 (2)°, and nearly parallel to the C2–C7 benzene ring, forming a dihedral angle of 5.8 (2)°

Intermolecular N1—H1···O2($-x$, $-y$, $1-z$) hydrogen bonds (Table 2) are formed between the amine and carbonyl groups, forming dimers (Fig. 2). The solvent dimethylformamide molecule shows positional disorder over two possible sites.

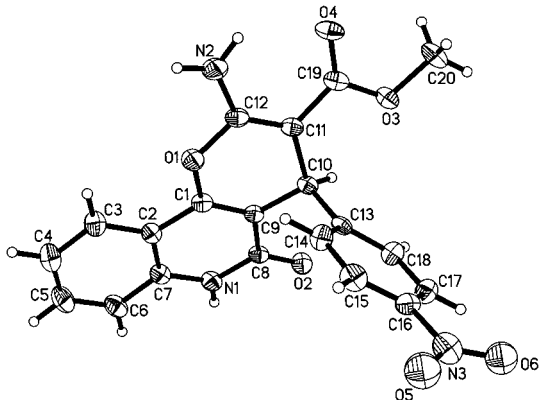


Figure 1
The molecular structure of (I), showing 30% probability displacement ellipsoids and the atom-numbering scheme. The dimethylformamide molecule has been omitted for clarity.

Experimental

The title compound, (I), was prepared by the reaction of methyl cyanoacetate (0.20 g, 2 mmol), 4-nitrobenzaldehyde (0.31 g, 2 mmol) and 4-hydroxyquinolin-2-one (0.32 g, 2 mmol) in the presence of KF–alumina (0.25 g) in EtOH at 353 K for 8 h (yield 91%, m.p. 548–550 K). Crystals of (I) suitable for X-ray diffraction were obtained by slow evaporation of a dimethylformamide solution. Analysis calculated: C 59.22, H 4.75, N 12.01%; found: C 59.39, H 4.87, N 12.30%. ^{1}H NMR (DMSO-d_6): δ 2.74 (*s*, 3H, CH_3), 2.89 (*s*, 3H, CH_3), 3.57 (*s*, 3H, CH_3), 4.84 (*s*, 1H, CH), 7.20 (*dd*, J = 8.0 Hz, J' = 2.0 Hz, 2H, ArH), 7.28–7.35 (*m*, 2H, ArH), 7.43 (*d*, J = 2.0 Hz, 1H, ArH), 7.48 (*d*, J = 8.4 Hz, 1H, ArH), 7.56–7.60 (*m*, 1H, ArH), 7.85 (*s*, 2H, NH_2), 7.96 (*s*, 1H, CHO), 7.98 (*d*, J = 8.0 Hz, 1H, ArH), 11.78 (*s*, 1H, NH); IR (cm^{-1}): 3380, 3275, 3203 (NH_2, NH), 3025 (Ar—H), 2943(C—H), 1683 (C═O), 1610, 1594, 1530, 1491 (phenyl ring).

Crystal data

$C_{20}H_{15}N_3O_6\cdot C_3H_7NO$	Z = 2
M_r = 466.45	D_x = 1.406 Mg m^{-3}
Triclinic, $P\overline{1}$	Mo $K\alpha$ radiation
a = 8.312 (1) Å	Cell parameters from 33 reflections
b = 11.696 (2) Å	θ = 3.3–15.3°
c = 11.705 (1) Å	μ = 0.11 mm^{-1}
α = 97.42 (1)°	T = 295 (2) K
β = 101.634 (9)°	Block, colorless
γ = 93.01 (1)°	0.58 × 0.36 × 0.24 mm
V = 1101.6 (3) Å^3	

Data collection

Siemens *P*4 diffractometer	θ_{max} = 25.8°
ω scans	$h = 0 \rightarrow 10$
Absorption correction: none	$k = -14 \rightarrow 14$
4659 measured reflections	$l = -14 \rightarrow 14$
4199 independent reflections	3 standard reflections
2437 reflections with $I > 2\sigma(I)$	every 97 reflections
R_{int} = 0.010	intensity decay: 4.4%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.1169P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)]$ = 0.065	$(\Delta/\sigma)_{max} < 0.001$
$wR(F^2)$ = 0.209	$\Delta\rho_{max}$ = 0.50 e Å^{-3}
S = 1.07	$\Delta\rho_{min}$ = −0.59 e Å^{-3}
4199 reflections	Extinction correction: *SHELXL*97
341 parameters	Extinction coefficient: 0.019 (5)
H atoms treated by a mixture of independent and constrained refinement	

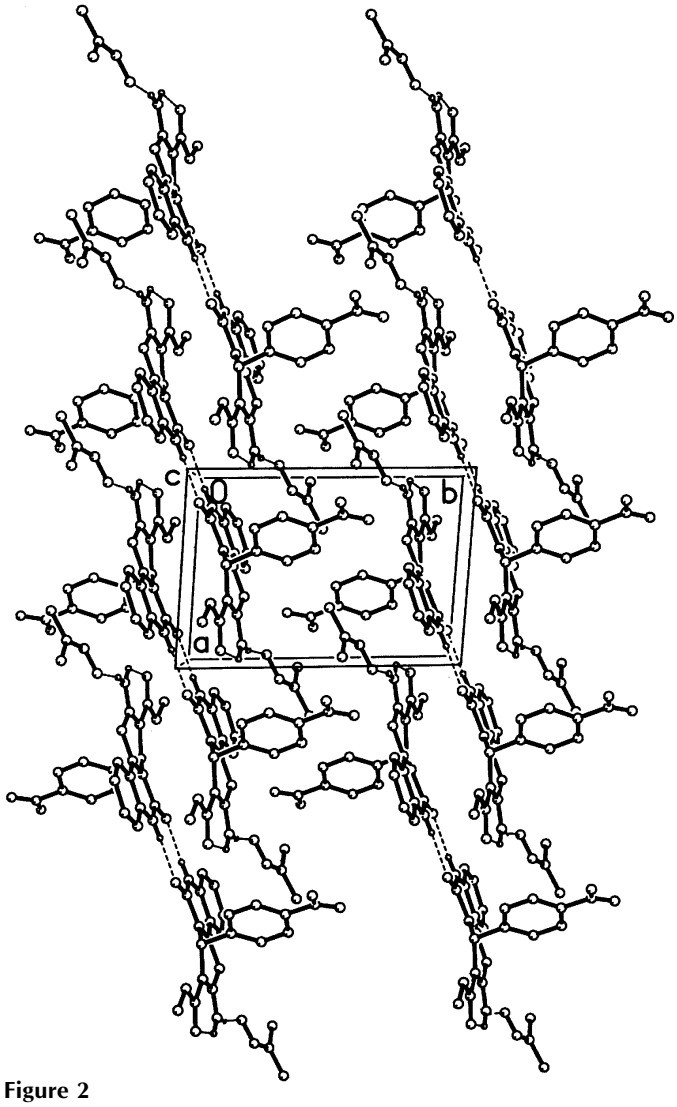


Figure 2
The molecular packing of (I). One of two possible sites of the disordered dimethylformamide molecule has been omitted for clarity. H atoms not involved in hydrogen bonding have been omitted.

Table 1
Selected geometric parameters (Å, °).

O1—C1	1.376 (3)	C1—C2	1.437 (4)
O1—C12	1.388 (3)	C2—C7	1.397 (4)
O2—C8	1.239 (3)	C8—C9	1.451 (4)
N1—C8	1.371 (3)	C9—C10	1.504 (4)
N1—C7	1.371 (4)	C10—C11	1.514 (4)
C1—C9	1.343 (4)	C11—C12	1.355 (4)
C1—O1—C12	118.1 (2)	C9—C10—C11	109.4 (2)
C8—N1—C7	125.2 (3)	C12—C11—C10	120.5 (2)
C9—C1—O1	121.9 (2)	C11—C12—O1	121.8 (2)
C9—C1—C2—C7	−1.3 (4)	O1—C1—C9—C10	4.7 (4)
C8—N1—C7—C2	4.0 (4)	N1—C8—C9—C1	−4.5 (4)
C1—C2—C7—N1	−3.3 (4)	C9—C10—C11—C12	23.5 (3)
C7—N1—C8—C9	0.0 (4)	C10—C11—C12—O1	−4.7 (4)
C2—C1—C9—C8	5.2 (4)	C1—O1—C12—C11	−17.0 (4)

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1N···O2^{i}	0.82 (4)	2.03 (4)	2.851 (3)	177 (3)
N2—H2A···O4	0.86	2.14	2.735 (4)	126
N2—H2B···O7^{ii}	0.86	2.05	2.901 (19)	169
N2—H2B···O7′^{ii}	0.86	2.07	2.92 (2)	172

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

The solvent dimethylformamide molecule shows positional disorder, and the occupancy factors of two possible sites, N4/O7/C21–C23 and N4′/O7′/C21′–C23′, are 49.7 (8) and 50.3 (8)%, respectively. The H atoms, except for H1N, were positioned geometrically and refined as riding, with C—H = 0.93–0.98 Å and N—H = 0.86 Å, and with U_{iso}(H) = 1.2U_{eq}(parent atom). H1N was located in a difference map and refined isotropically.

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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