Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

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

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

[a]Department of Chemistry, Xuzhou Normal University, Xuzhou 221116, People's Republic of China, and [b]School of Chemical Engineering, China University of Mining and Technology, Xuzhou 221008, 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) = 0.003 Å
Disorder in solvent or counterion
R factor = 0.041
wR factor = 0.108
Data-to-parameter ratio = 11.8

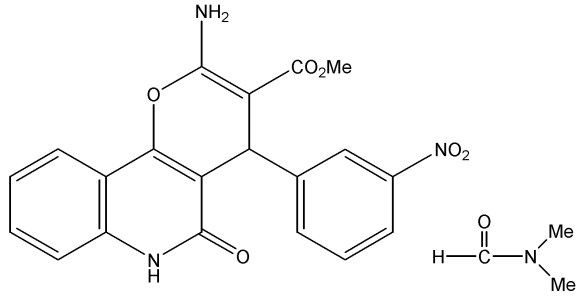
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Received 23 August 2004
Accepted 22 September 2004
Online 30 September 2004

The title compound, $C_{20}H_{15}N_3O_6\cdot C_3H_7NO$, was synthesized by the reaction of methyl 2-cyano-3-(3-nitrophenyl)acrylate and 4-hydroxyquinolin-2-one in ethanol, catalysed by KF–alumina. 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, as such compounds exhibit antibacterial activity (Madkour *et al.*, 2001), are used as anti-hypertensive agents (Jolivet *et al.*, 1996) and possess moderate acetylcholinesterase inhibitory activity (Marco *et al.*, 2001). The utility of fluoride salts as potential bases in a variety of synthetic reactions has been recognized in recent years. 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), prepared in a cyclization reaction catalysed by KF–alumina.



(I)

In (I), the atoms of the central pyridine ring are coplanar, with atoms N1, C1, C2, C7, C8 and C9 deviating from the mean plane by −0.019 (2), −0.017 (2), -0.009 (2), 0.027 (2), −0.007 (2) and 0.025 (2) Å, respectively. 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/C12 by 0.291 (2) and 0.168 (2) Å, respectively. A similar distortion was observed in ethyl 2-amino-4-(3-nitrophenyl)-1,4-dihydro-2*H*-pyrano[3,2-*h*]quinoline-3-carboxylate (Wang *et al.*, 2004) and 9-(2-hydroxy-4,4-dimethyl-6-oxocyclohex-1-enyl)-3,3,7-trimethyl-1,2,3,4-hexahydro-9*H*-xanthen-1-one (Li *et al.*, 2004). The basal plane of the pyran ring is nearly perpendicular to benzene ring C13–C18, forming a dihedral angle of 87.9 (2)°, and nearly parallel to benzene ring C2–C7, forming a dihedral angle of 5.9 (2)°. Intermolecular N1—H1···O2($2-x$, $1-y$, $2-z$) hydrogen bonds (Table 2) are formed in pairs between

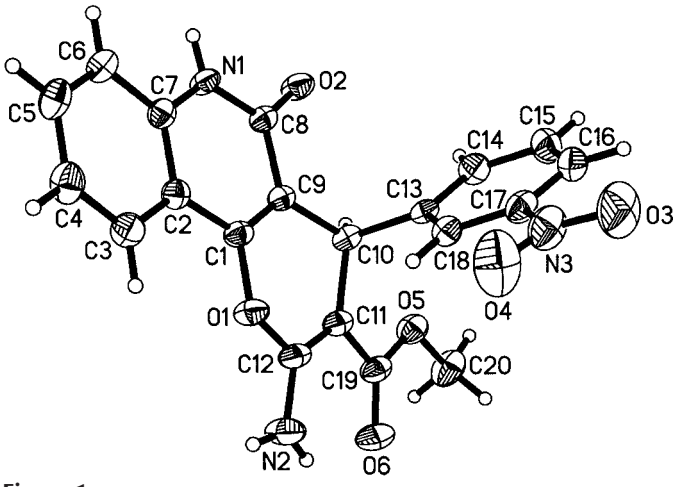


Figure 1
The structure of (I), showing the atom-numbering scheme and displacement ellipsoids drawn at the 30% probability level. H atoms are drawn as spheres of arbitrary radius. The dimethylformamide molecule of crystallization has been omitted for clarity.

the amino and carbonyl groups, resulting in dimers. These link to two molecules of dimethylformamide by a further intermolecular N2—H2*A*···O7 contact (Fig. 2). The solvent dimethylformamide molecule shows positional disorder over two possible sites.

Experimental

The title compound, (I), was prepared by the reaction of methyl 2-cyano-3-(3-nitrophenyl)acrylate (0.46 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 86%, m.p. 541–542 K). Crystals of (I) suitable for X-ray diffraction were obtained by slow evaporation of a dimethylformamide solution. Elemental analysis calculated: C 59.22, H 4.75, N 12.01%; found: C 60.02, H 4.68, N 11.99%; ^{1}H NMR (DMSO-d_6): δ 2.84 (*s*, 3H, CH_3), 3.01 (*s*, 3H, CH_3), 3.56 (*s*, 3H, CH_3), 4.96 (*s*, 1H, CH), 7.28–7.34 (*m*, 2H, ArH), 7.51–7.60 (*m*, 2H, ArH), 7.71 (*d*, *J* = 7.6 Hz, 1H, ArH), 7.88 (*s*, 2H, NH_2), 7.92 (*s*, 1H, CHO), 8.00 (*d*, *J* = 7.6 Hz, 2H, ArH), 8.05 (*s*, 1H, ArH), 11.77 (*s*, 1H, NH); IR (cm^{-1}): 3392, 3283, 3193 (NH_2, NH), 3019 (Ar–H), 2943, 2853 (C—H), 1683 (C═O), 1612, 1574, 1527, 1489 (benzene ring).

Crystal data

$C_{20}H_{15}N_3O_6\cdot C_3H_7NO$
M_r = 466.45
Triclinic, $P\overline{1}$
a = 8.216 (1) Å
b = 11.695 (2) Å
c = 12.204 (2) Å
α = 77.44 (1)°
β = 89.00 (1)°
γ = 78.40 (1)°
V = 1120.8 (3) Å^3
Z = 2
D_x = 1.382 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 33 reflections
θ = 2.8–14.8°
μ = 0.10 mm^{-1}
T = 295 (2) K
Block, colorless
0.56 × 0.34 × 0.18 mm

Data collection

Siemens *P*4 diffractometer
ω scans
4712 measured reflections
4242 independent reflections
2583 reflections with $I > 2\sigma(I)$
R_{int} = 0.010
θ_{max} = 25.8°
$h = 0 \rightarrow 9$
$k = -13 \rightarrow 13$
$l = -14 \rightarrow 14$
3 standard reflections
every 97 reflections
intensity decay: 3.2%

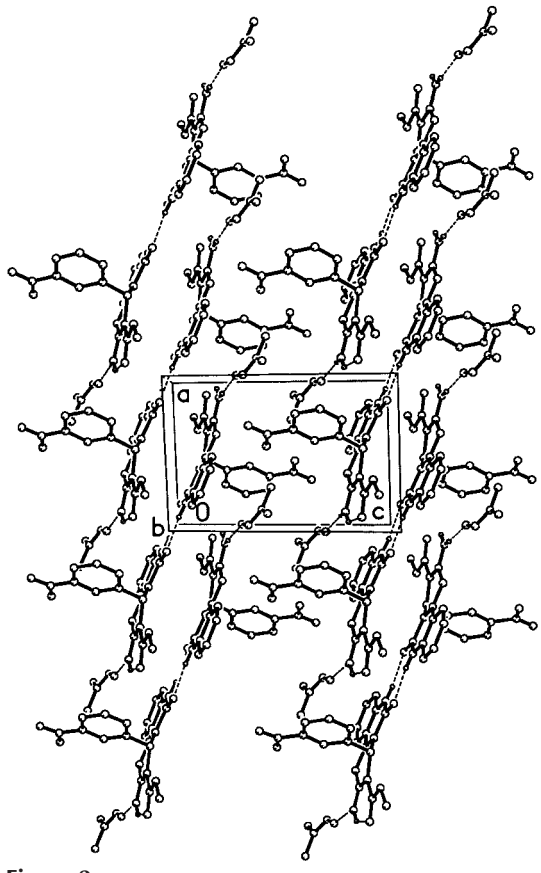


Figure 2
A molecular packing diagram of (I). One of two possible sites of the disordered dimethylformamide molecule has been omitted for clarity.

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.041
$wR(F^2)$ = 0.108
S = 0.90
4242 reflections
361 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0606P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.24 e Å^{-3}
$\Delta\rho_{min}$ = −0.16 e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.016 (2)

Table 1
Selected geometric parameters (Å, °).

O1—C12	1.379 (2)	C1—C2	1.436 (2)
O1—C1	1.379 (2)	C2—C7	1.399 (2)
O2—C8	1.245 (2)	C8—C9	1.450 (2)
N1—C8	1.360 (2)	C9—C10	1.502 (2)
N1—C7	1.375 (2)	C10—C11	1.515 (2)
C1—C9	1.347 (2)	C11—C12	1.360 (3)
C12—O1—C1	118.02 (14)	C9—C10—C11	109.42 (15)
C8—N1—C7	124.92 (15)	C12—C11—C10	120.44 (16)
C9—C1—O1	122.00 (16)	C11—C12—O1	122.12 (16)
C9—C1—C2—C7	1.0 (3)	O1—C1—C9—C10	−4.3 (3)
C8—N1—C7—C2	−4.7 (3)	N1—C8—C9—C1	2.9 (2)
C1—C2—C7—N1	3.3 (2)	C9—C10—C11—C12	−22.9 (2)
C7—N1—C8—C9	1.5 (3)	C10—C11—C12—O1	5.0 (3)
C2—C1—C9—C8	−4.1 (3)	C1—O1—C12—C11	16.1 (3)

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O2^{i}	0.86	1.99	2.8460 (19)	173
N2—H2A···O7	0.84 (2)	2.10 (2)	2.914 (7)	163 (2)
N2—H2A···O7′	0.84 (2)	2.16 (3)	3.00 (2)	171 (2)
N2—H2B···O6	0.83 (2)	2.13 (2)	2.759 (3)	133 (2)

Symmetry code: (i) $2-x, 1-y, 2-z$.

The solvent dimethylformamide molecule shows positional disorder, and the occupancy factors of the two possible sites, *viz*. N4/O7/C21–C23 and N4′/O7′/C21′–C23′, are 64.9 (8) and 35.1 (8)%, respectively. Amine H atoms H2*A* and H2*B* were refined isotropically. All other H atoms were placed in idealized positions and refined as riding on their carrier atoms, with C—H = 0.91–0.98 Å and N—H = 0.86 Å, and U_{iso}(H) = 1.2U_{eq}(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*.

We thank the Foundation of the 'Surpassing Project' of Jiangsu Province and the Natural Science Foundation (No. 04 KJB150139) of the Education Committee of Jiangsu Province for financial support.

References

Clark, J. H. (1980). *Chem. Rev.* **80**, 429–452.
Li, Y. L., Wang, X. S., Shi, D. Q., Tu, S. J. & Zhang, Y. (2004). *Acta Cryst.* E**60**, o1439–o1441.
Jolivet, C., Rivalle, C. & Bisagni, E. (1996). *Heterocycles*, **43**, 995–1006.
Madkour, H. M. F., Mahmoud, M. R., Sakr, A. M. & Habashy, M. M. (2001). *Sci. Pharm.* **69**, 33–52.
Marco, J. L., Delos, R. C., Carreiras, M. C., Banos, J. E., Badia, A. & Vivas, N. M. (2001). *Bioorg. Med. Chem.* **9**, 727–732.
Sheldrick, G. M. (1997). *SHELXTL.* Version 5.1. Bruker AXS Inc., Madison, Wisconsin, USA.
Siemens (1994). *XSCANS.* Version 2.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Wang, X. S., Shi, D. Q. & Tu, S. J. (2004). *Chin. J. Struct. Chem.* **23**, 131–134.