Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

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

Xiangshan Wang,[a]* Zhaosen Zeng,[a] Daqing Shi,[a] Xianyong Wei[b] and Zhimin 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 of 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 = 0.054
wR factor = 0.170
Data-to-parameter ratio = 14.0

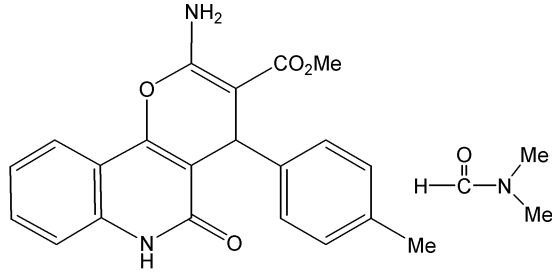
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Received 3 August 2004
Accepted 19 August 2004
Online 28 August 2004

The title compound, $C_{24}H_{25}N_3O_5$, was synthesized by the reaction of methyl 2-cyano-3-(4-methylphenyl)-1-acrylate and 4-hydroxyquinolin-2-one in the presence of triethylbenzylammonium chloride in aqueous media. 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 are high-affinity high-selectivity modulators of steroid receptors and, in particular, are agonists or antagonists of progesterone and androgen receptors (Jones *et al.*, 1998). We report here the crystal structure of the title compound, (I). Its aqueous synthesis (see *Experimental*) was inspired by the work of Breslow & Rideout (1980) who rediscovered the use of water as a solvent in organic chemistry.



(I)

In (I), the outer 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 the atoms C1/C9/C11/C12 by 0.290 (2) and 0.167 (2) Å, respectively. Similar distortions were observed in ethyl 2-amino-4-(3-nitrophenyl)-1,4-dihydro-2*H*-pyrano[3,2-*h*]-quinolin-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 the C13—C18 phenyl ring, forming a dihedral angle of 84.9 (2)°.

Intermolecular N1—H1···O2($-x$, $-y$, $1-z$) cyclic hydrogen bonds (Table 2) are formed between the amino and carbonyl groups, forming dimers (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-(4-methylphenyl)-1-acrylate (0.40 g, 2 mmol) and 4-hydroxyquinolin-2-one (0.32 g, 2 mmol) in the presence of

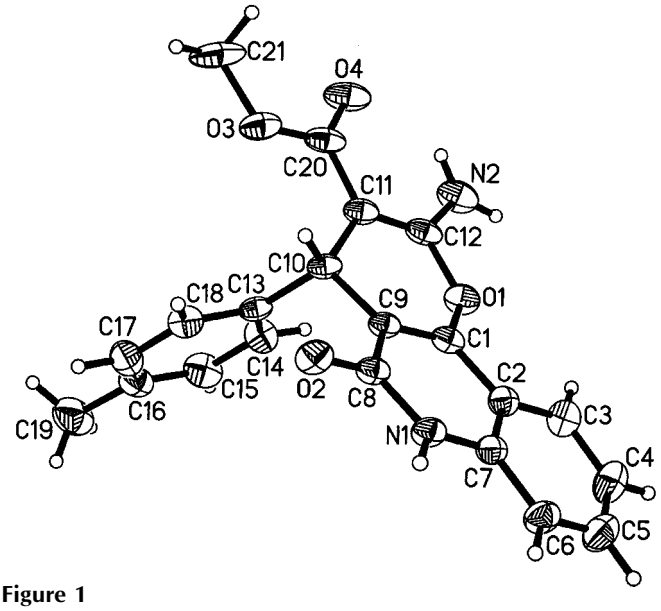


Figure 1
The molecular structure of (I), showing 30% probability displacement ellipsoids and the atom-numbering scheme. Add H atoms are represented by small spheres. The dimethylformamide molecule of crystallization has been omitted for clarity.

triethylbenzylammonium chloride (0.1 g) in water at 363 K for 8 h (yield 95%, m.p. 535–537 K). Crystals of (I) suitable for X-ray diffraction were obtained by slow evaporation of a dimethylformamide solution. Elemental analysis calculated: C 66. 19, H 5.79, N 9.65%; found: C 66. 32, H 5.85, N 9.43%. ^{1}H NMR (DMSO-d_6): δ 2.20 (*s*, 3H, CH_3), 2.84 (*s*, 3H, CH_3), 3.01 (*s*, 3H, CH_3), 3.56 (*s*, 3H, CH_3), 4.82 (*s*, 1H, CH), 7.01 (*d*, J = 8.4 Hz, 2H, ArH), 7.12 (*d*, J = 8.4 Hz, 2H, ArH), 7.27–7.35 (*m*, 2H, ArH), 7.53–7.58 (*m*, 1H, ArH), 7.74 (*s*, 2H, NH_2), 7.92 (*s*, 1H, CHO), 7.96 (*d*, J = 7.2 Hz, 1H, ArH), 11.70 (*s*, 1H, NH); IR (cm^{-1}): 3412, 3279, 3193 (NH_2, NH), 3061, 3010 (Ar—H), 2952, 2850 (C—H), 1672 (C═O), 1598, 1581, 1430 (phenyl ring).

Crystal data

$C_{21}H_{18}N_2O_4{\cdot}C_3H_7NO$
M_r = 435.47
Triclinic, $P\overline{1}$
a = 8.577 (1) Å
b = 11.420 (2) Å
c = 11.729 (1) Å
α = 96.28 (1)°
β = 102.43 (1)°
γ = 92.00 (1)°
V = 1113.2 (3) Å^3
Z = 2
D_x = 1.299 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 39 reflections
θ = 2.7–14.2°
μ = 0.09 mm^{-1}
T = 295 (2) K
Block, colorless
0.56 × 0.48 × 0.36 mm

Data collection

Siemens $P4$ diffractometer
ω scans
Absorption correction: none
4862 measured reflections
4361 independent reflections
2298 reflections with $I > 2\sigma(I)$
R_{int} = 0.010
θ_{max} = 26.0°
$h = 0 \rightarrow 10$
$k = -13 \rightarrow 13$
$l = -14 \rightarrow 14$
3 standard reflections
every 97 reflections
intensity decay: 3.5%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.054
$wR(F^2)$ = 0.170
S = 0.90
4361 reflections
311 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.103P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.55 e Å^{-3}
$\Delta\rho_{min}$ = −0.18 e Å^{-3}
Extinction correction: *SHELXTL*
Extinction coefficient: 0.015 (3)

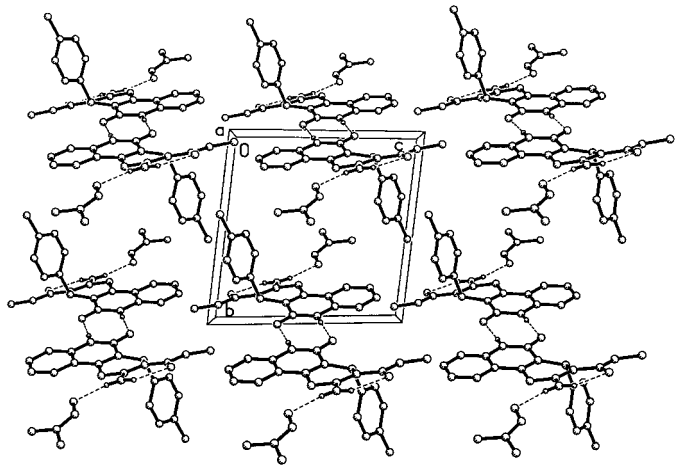


Figure 2
The molecular packing of (I). Hydrogen bonds are indicated by dashed lines. One of two possible sites of the disordered dimethylformamide molecule has been omitted for clarity.

Table 1
Selected geometric parameters (Å, °).

O1—C1	1.379 (3)	C1—C2	1.434 (3)
O1—C12	1.387 (3)	C2—C7	1.400 (3)
O2—C8	1.244 (3)	C8—C9	1.456 (3)
N1—C8	1.364 (3)	C9—C10	1.498 (3)
N1—C7	1.368 (3)	C10—C11	1.505 (3)
C1—C9	1.351 (3)	C11—C12	1.354 (3)
C1—O1—C12	117.64 (19)	C9—C10—C11	109.80 (19)
C8—N1—C7	125.22 (19)	C12—C11—C10	120.3 (2)
C9—C1—O1	121.7 (2)	C11—C12—O1	122.6 (2)
C9—C1—C2—C7	−1.1 (3)	O1—C1—C9—C10	5.3 (3)
C8—N1—C7—C2	4.2 (3)	N1—C8—C9—C1	−4.7 (3)
C1—C2—C7—N1	−3.6 (3)	C9—C10—C11—C12	22.8 (3)
C7—N1—C8—C9	0.1 (3)	C10—C11—C12—O1	−4.5 (3)
C2—C1—C9—C8	5.3 (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	2.853 (2)	180
N2—H2A···O4	0.86	2.16	2.740 (3)	125
N2—H2B···O5^{ii}	0.86	2.00	2.851 (9)	172
N2—H2B···O5′^{ii}	0.86	2.12	2.97 (3)	173

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, N3/O5/C22–C24 and N3′/O5′/C22′–C24′, are 71.6 (4) and 28.4 (4)%, respectively. The H atoms were calculated geometrically and refined as riding, with C—H = 0.91–0.98 Å and N—H = 0.86 Å, and with U_{iso}(H) = 1.2U_{eq}(parent atom). The maximum difference-density peak is 1.16 Å from atom C21.

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 of the Education Committee of Jiangsu Province for financial support.

References

Breslow, R. & Rideout, D. C. (1980). *J. Am. Chem. Soc.* **102**, 7816–7817.

Jones, T. D., Zhi, L., Edward, J. P., Tegly, C. M. & West, S. J. (1998). US Patent US 5 696 127.

Li, Y.-L., Wang, X.-S., Shi, D.-Q., Tu, S.-J. & Zhang, Y. (2004). *Acta Cryst.* E**60**, o1439–o1441.

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.