Crystal Structure of 7-(4-Fluorophenyl)-5,6,7,14-tetrahydroquinolino[4,3-*b*]-benzo[*f*]quinolin-6-one *N,N*-Dimethylformamide Solvate

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The crystal structure of 7-(4-fluorophenyl)-5,6,7,14-tetrahydroquinolino[4,3-*b*]-benzo[*f*]-quinolin-6-one *N,N*-dimethylformamide solvate was determined by X-ray diffraction. The title compound **1**, C₂₉H₂₄FN₃O₂, is monoclinic, space group *P*2₁/*c*, *a* = 9.5653(12), *b* = 24.394(3), *c* = 10.7387(15) Å, β = 111.978(2)°, *Z* = 4, *V* = 2323.6(5) Å³. The central 1,4-dihydropyridine ring adopts a boat confirmation. The intermolecular hydrogen bonds of N-H...O link the molecules forming the dimmers and another amino group connects the two solvent molecules with the dimmer forming the N-H...O hydrogen bonds.

(Received November 22, 2005; Accepted February 13, 2006; Published on web May 31, 2006)

Dihydroquinoline moieties can be found in a variety of natural products¹ and in a large number of compounds that display biological activity, for example, antibacterial,² antidiabetic and anti-inflammatory activities.³ Moreover different conformations exist with different activities.⁴ In order to establish the conformational aspects of these potential biologically active compounds, the crystal structure of 7-(4-fluorophenyl)-5,6,7,14-tetrahydroquinolino[4,3-*b*]-benzo[*f*]quinolin-6-one *N,N*-dimethylformamide solvate was examined (Fig. 1).

The title compound was synthesized by the reaction of *N*-arylidenenaphthalen-2-amine and 4-hydroxyquinolin-2-one in water in the presence of TEBA (triethylbenzyl ammonium chloride) at 100°C. Crystals suitable for X-ray diffraction were obtained by slow evaporation of a DMF solution. m.p. >300°C. IR (KBr, ν, cm⁻¹): 3320, 3061, 2913, 1667, 1642, 1601, 1590, 1563, 1515, 1499, 1465, 1390, 1288, 1257, 1212, 1155, 1094, 846, 838, 817, 738; ¹H NMR (DMSO-*d*₆, δ, ppm): 2.73 (s, 3H, CH₃), 2.89 (s, 3H, CH₃), 6.12 (s, 1H, CH), 6.98 (d, *J* = 8.8 Hz, 2H, ArH), 7.25 – 7.39 (m, 5H, ArH), 7.44 – 7.53 (m, 2H, ArH), 7.73 (d, *J* = 8.8 Hz, 1H, ArH), 7.87 (d, *J* = 8.8 Hz, 2H, ArH), 7.95 (s, 1H, CHO), 7.99 (d, *J* = 8.8 Hz, 1H, ArH), 8.32 (d, *J* = 8.4 Hz, 1H, ArH), 9.63 (s, 1H, NH), 11.32 (s, 1H, NH). Anal. calcd for C₂₉H₂₄FN₃O₂: C 74.82, H 5.20, N 9.03; found C 74.75,

H 5.38, N 8.97. The crystal and experimental details are given in Table 1. The structure was solved by a direct method and refined by full matrix least squares to a final reliability value of 0.0429. The non-hydrogen atoms were refined anisotropically. The hydrogen atoms were positioned geometrically and refined as riding [C-H = 0.93 – 0.98 Å and *U*_{iso}(H) = 1.2*U*_{eq}(C)], except

Table 1 Crystallographic and experimental data for **1**

Empirical formula	C ₂₉ H ₂₄ FN ₃ O ₂
CCDC deposit no.	294907
Color/shape	Pale yellow/Block
Formula weight	465.51
Temperature	294(2)K
Crystal system	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>
Unit cell dimensions	<i>a</i> = 9.5653(12) Å <i>b</i> = 24.394(3) Å <i>c</i> = 10.7387(15) Å β = 111.978(2)°
Volume	2323.6 Å ³
<i>Z</i>	4
Density (calculated), Mg/m ³	1.331
Absorption coefficient, mm ⁻¹	0.090
<i>F</i> (0 0 0)	976
Crystal size	0.36 × 0.28 × 0.22 mm
Theta range for data collection	1.67 to 26.38°
Limiting indices	−11 ≤ <i>h</i> ≤ 11, −18 ≤ <i>k</i> ≤ 30, −13 ≤ <i>l</i> ≤ 13
Reflections collected	12953
Independent reflections	4697 [<i>R</i> (int) = 0.0356]
Data/restraints/parameters	4697/0/327
Goodness-of-fit, on <i>F</i> ²	1.009
Final <i>R</i> indices [3071 refs. <i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0429, <i>wR</i> 2 = 0.1026
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0760, <i>wR</i> 2 = 0.1222
Largest diff peak and hole	0.190 and −0.162 e Å ⁻³
Measurement	CCD area detector
Refinement	full-matrix least square on <i>F</i> ²

Fig. 1 Chemical diagram of title compound **1**.

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Table 2 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\times 10^3 \text{ \AA}^2$) for non-hydrogen atoms

Atom	x	y	z	U_{eq}
F(1)	3461(2)	2247(1)	7144(1)	89(1)
O(1)	-606(1)	4465(1)	5840(1)	49(1)
N(1)	1176(2)	5119(1)	6712(2)	42(1)
N(2)	1980(2)	4572(1)	10548(2)	43(1)
C(1)	2292(2)	5374(1)	7761(2)	40(1)
C(2)	3127(2)	5799(1)	7496(2)	52(1)
C(3)	4232(2)	6054(1)	8529(2)	58(1)
C(4)	4528(2)	5902(1)	9847(2)	57(1)
C(5)	3718(2)	5484(1)	10118(2)	50(1)
C(6)	2594(2)	5208(1)	9080(2)	39(1)
C(7)	1751(2)	4742(1)	9275(2)	37(1)
C(8)	748(2)	4467(1)	8195(2)	36(1)
C(9)	383(2)	4675(1)	6861(2)	38(1)
C(10)	69(2)	3922(1)	8357(2)	36(1)
C(11)	939(2)	3453(1)	8023(2)	37(1)
C(12)	557(2)	3263(1)	6716(2)	50(1)
C(13)	1398(2)	2857(1)	6414(2)	60(1)
C(14)	2606(2)	2645(1)	7426(2)	56(1)
C(15)	3019(2)	2813(1)	8724(2)	56(1)
C(16)	2172(2)	3218(1)	9013(2)	46(1)
C(17)	75(2)	3868(1)	9767(2)	36(1)
C(18)	-838(2)	3468(1)	10073(2)	39(1)
C(19)	-1879(2)	3133(1)	9081(2)	47(1)
C(20)	-2730(2)	2750(1)	9407(2)	56(1)
C(21)	-2576(2)	2678(1)	10746(2)	59(1)
C(22)	-1578(2)	2987(1)	11730(2)	54(1)
C(23)	-686(2)	3389(1)	11430(2)	43(1)
C(24)	357(2)	3714(1)	12444(2)	49(1)
C(25)	1197(2)	4100(1)	12142(2)	46(1)
C(26)	1061(2)	4175(1)	10796(2)	38(1)
O(2)	3944(2)	5053(1)	3190(2)	88(1)
N(3)	5066(2)	5842(1)	4131(2)	58(1)
C(27)	3981(2)	5476(1)	3800(2)	64(1)
C(28)	6397(3)	5747(1)	3834(3)	96(1)
C(29)	5052(4)	6327(1)	4902(3)	110(1)

U_{eq} is defined as one third of the trace of orthogonalized U_{ij} tensor.

Fig. 2 Molecular structure of **1** showing 50% probability displacement ellipsoids.

for H1 and H2. The atomic coordinates of the non-hydrogen atoms are presented in Table 2.

The structure of **1** is shown in Fig. 2. The X-ray crystal structure determination indicates that the central 1,4-dihydropyridine ring is slightly distorted and adopts a boat conformation. Atoms C10 and N2 deviate from the basal plane defined by the atoms C7/C8/C17/C26 by 0.296(2) and 0.110(2) Å, respectively. Similar distortions were observed in the structures of 3,3,6,6-tetramethyl-9-(4-chlorophenyl)-10-(4-methylphenyl)-1,2,3,4,5,6,7,8,9,10-decahydroacridine-1,8-dione and 7,7-dimethyl-2,4-diphenyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline.⁵ The 1,4-dihydropyridine ring is nearly

Table 3 Selected bond lengths (Å) and selected bond angles (°) for **1**

F(1)-C(14)	1.375(2)	C(7)-C(8)	1.372(2)
O(1)-C(9)	1.2577(19)	C(8)-C(9)	1.434(2)
N(1)-C(9)	1.366(2)	C(8)-C(10)	1.519(2)
N(1)-C(1)	1.376(2)	C(10)-C(17)	1.517(2)
N(1)-H(1)	0.98(2)	C(10)-C(11)	1.533(2)
N(2)-C(7)	1.365(2)	N(2)-H(2)	0.92(2)
N(2)-C(26)	1.399(2)	C(6)-C(7)	1.454(2)
C(9)-N(1)-C(1)	123.85(15)	N(1)-C(9)-C(8)	117.33(15)
C(7)-N(2)-C(26)	121.55(15)	C(17)-C(10)-C(8)	110.37(13)
N(1)-C(1)-C(6)	120.17(15)	C(17)-C(10)-C(11)	111.73(13)
N(1)-C(1)-C(2)	119.62(16)	C(8)-C(10)-C(11)	109.39(12)
C(1)-C(6)-C(7)	117.22(15)	C(13)-C(14)-F(1)	119.41(18)
C(5)-C(6)-C(7)	124.39(16)	C(15)-C(14)-F(1)	117.96(19)
N(2)-C(7)-C(8)	119.92(14)	N(2)-C(26)-C(25)	117.44(15)
N(2)-C(7)-C(6)	119.38(15)	O(1)-C(9)-N(1)	119.39(15)
C(8)-C(7)-C(6)	120.70(15)	O(1)-C(9)-C(8)	123.27(15)
C(7)-C(8)-C(9)	120.23(14)	C(9)-C(8)-C(10)	118.05(14)
C(7)-C(8)-C(10)	121.61(14)		

Table 4 Classical hydrogen bonds geometry for **1**

(D-H...A)	D-H (Å)	H...A (Å)	D...A (Å)	D-H...A (°)
N1-H1 ... O1#1	0.98(2)	1.80(2)	2.7787(19)	173.4(19)
O2-H2 ... O2#2	0.92(2)	2.09(2)	2.994(2)	167.1(17)

Symmetry codes #1: $-x, -y + 1, -z + 1$; #2: $x, y, z + 1$.

perpendicular to 4-fluorophenyl ring, forming a dihedral angle of 85.2(1)°, and nearly parallel to the naphthalene ring and another quinoline ring, forming dihedral angles of 5.7(1)° and 6.5(1)°, respectively. From Table 3, it is easy to find that the distance from H1 to O1 in the adjacent molecules is 1.80(2) Å, the angle of N1-H1...O1 is 173.4(19)°. These results suggest that H1 can form an intermolecular hydrogen bond with the O1 atom in adjacent molecules forming dimers. On the other hand, another hydrogen atom H2 bonded to N2 forms a different hydrogen bond N2-H2...O2, and the distance from H2 to O2 in the adjacent molecules is 2.09(2) Å, and the angle of N2-H2...O2 is 167.1(17)°. The above hydrogen bond N2-H2...O2 connects the molecule with the vicinal solvent molecule of DMF in the crystal.

Acknowledgements

We are grateful to the Foundation (04KJB150139) of the Education Committee of Jiangsu Province for financial support.

References

1. A. Balayer, T. Sevenet, H. Schaller, A. Hamid, A. Hadi, A. Chiaroni, C. Riche, and M. Pais, *Nat. Prod. Lett.*, **1993**, 2, 61.
2. J. V. Johnson, *J. Med. Chem.*, **1989**, 32, 19429.
3. G. De Nanteuil, J. Duhault, D. Ravel, and Y. Herve, **1993**, EP 528734.
4. A. Morales, E. Ochoa, and M. Suarez, *J. Heterocycl. Chem.*, **1996**, 33, 103.
5. a) X. S. Wang, D. Q. Shi, and S. J. Tu, *Acta Cryst.*, **2003**, E59, o1139. b) X. S. Wang, D. Q. Shi, S. J. Tu, and C. S. Yao, *J. Chem. Cryst.*, **2002**, 32, 381.