Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

Ethyl 2-amino-4-(4-fluorophenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4*H*-benzo[*b*]pyran-3-carboxylate

Daqing Shi,* Shu Zhang, Xiangshan Wang and Qiya Zhuang

Department of Chemistry, Xuzhou Normal University, Xuzhou 221116, People's Republic of China

Correspondence e-mail: dqshi@163.com

Received 18 August 2003
Accepted 9 September 2003
Online 18 September 2003

Key indicators

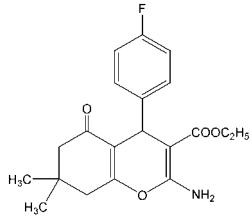
Single-crystal X-ray study
T = 296 K
Mean σ(C–C) = 0.003 Å
R factor = 0.040
wR factor = 0.114
Data-to-parameter ratio = 13.4

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

The title compound, $C_{20}H_{22}FNO_4$, was synthesized by the reaction of 4-fluorobenzaldehyde with 5,5-dimethyl-1,3-cyclohexanedione and ethyl cyanoacetate. The pyran ring adopts a boat conformation, while the fused six-membered ring adopts a distorted boat conformation.

Comment

Benzopyrans possess a wide range of pharmacological activities (Bloxham *et al.*, 1994; Nawwar *et al.*, 1991; Zamocka *et al.*, 1991). The use of water as a solvent in organic chemistry was rediscovered in the 1980s (Breslow & Rideout, 1980). As part of our program aimed at developing new selective and environmentally friendly methodologies for the preparation of fine chemicals (Shi *et al.*, 2003), we carried out a reaction employing water as the reaction medium. We report here the X-ray crystal structure of the title compound, (I).



(I)

The pyran ring adopts a boat conformation (Fig. 1 and Table 1); atoms C8, C13, C14 and C15 are coplanar, with atoms O1 and C7 deviating from the plane by 0.120 (1) and 0.258 (1) Å, respectively. A similar distortion was observed in the structure of 2-amino-7,7-dimethyl-4-(3-fluorophenyl)-5-oxo-3-ethoxycarbonyl-5,6,7,8-tetrahydro-4*H*-benzo(*b*)pyran (Sharanina *et al.*, 1986). In addition, the N—C14 bond length of 1.330 (2) Å is shorter than the typical Csp^2—N distance (Lorente *et al.*, 1995). The fused six-membered ring adopts a distorted boat conformation; atoms C8, C9, C10 and C13 are coplanar, while atoms C11 and C12 deviate from the plane by 0.761 (1) and 0.212 (1) Å, respectively. Molecules are linked by N—H···O hydrogen bonds (Table 2 and Fig. 2).

Experimental

The title compound, (I) (m.p. 433–434 K), was prepared by the reaction of 4-fluorobenzaldehyde with 5,5-dimethyl-1,3-cyclohexanedione and ethyl cyanoacetate in the presence of triethylbenzylammonium chloride in water. Single crystals of (I) suitable for X-ray diffraction were obtained by slow evaporation of an ethanol solution.

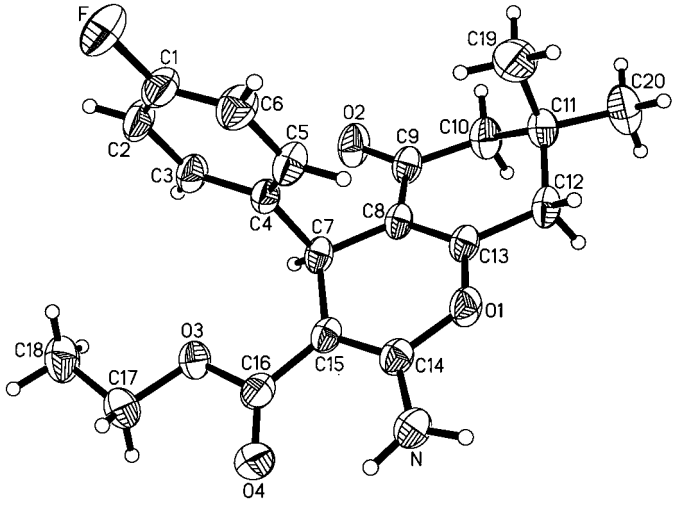


Figure 1
The molecular structure of (I), showing 50% probability displacement ellipsoids and the atom-numbering scheme.

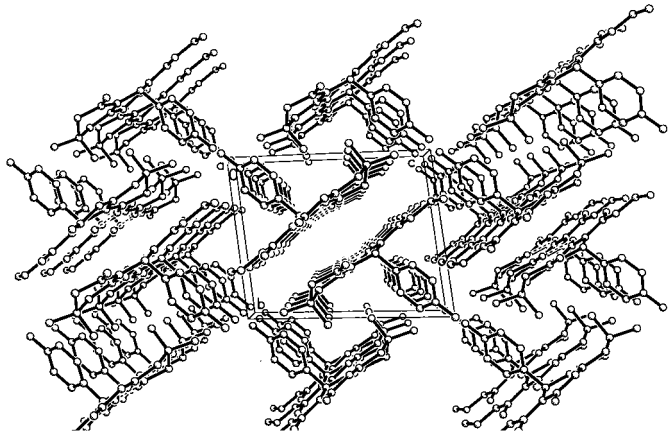


Figure 2
The molecular packing in the crystal structure of (I).

Crystal data

$C_{20}H_{22}FNO_4$
M_r = 359.39
Triclinic, $P\overline{1}$
a = 8.266 (1) Å
b = 9.773 (1) Å
c = 12.375 (2) Å
α = 81.40 (1)°
β = 73.41 (1)°
γ = 82.15 (1)°
V = 942.6 (2) Å^3
Z = 2
D_x = 1.266 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 32 reflections
θ = 3.1–15.1°
μ = 0.09 mm^{-1}
T = 296 (2) K
Block, colorless
0.50 × 0.46 × 0.40 mm

Data collection

Siemens $P4$ diffractometer
ω scans
Absorption correction: ψ scan (*XSCANS*; Siemens, 1994)
T_{min} = 0.937, T_{max} = 0.964
3694 measured reflections
3316 independent reflections
2258 reflections with $I > 2\sigma(I)$
R_{int} = 0.008
θ_{max} = 25.0°
$h = 0 \rightarrow 9$
$k = -11 \rightarrow 11$
$l = -14 \rightarrow 14$
3 standard reflections
every 97 reflections
intensity decay: 2.3%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.040
$wR(F^2)$ = 0.114
S = 1.00
3316 reflections
247 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0652P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.20 e Å^{-3}
$\Delta\rho_{min}$ = −0.19 e Å^{-3}
Extinction correction: *SHELXTL*
Extinction coefficient: 0.040 (4)

Table 1
Selected geometric parameters (Å, °).

O1—C13	1.3686 (19)	C7—C15	1.514 (2)
O1—C14	1.3770 (19)	C8—C13	1.336 (2)
N—C14	1.330 (2)	C14—C15	1.359 (2)
C7—C8	1.505 (2)		
C13—O1—C14	118.45 (12)	C15—C14—O1	122.24 (15)
N—C14—O1	109.95 (15)	C14—C15—C7	120.74 (15)
C15—C7—C8—C9	159.77 (13)	N—C14—C15—C16	−1.7 (3)
C13—C8—C9—C10	3.3 (2)	C4—C7—C15—C14	−103.32 (17)
C11—C12—C13—C8	15.1 (2)		

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

D—H···A	D—H	H···A	D···A	D—H···A
N—H1B···O2^{i}	0.87 (2)	2.03 (2)	2.889 (2)	170.6 (19)
N—H1A···O4	0.90 (2)	2.04 (2)	2.688 (2)	128.1 (18)

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

The amino H1*A* and H1*B* atoms were refined isotropically. The positions of the other H atoms were fixed and distances to H atoms were set by *SHELXTL* (Sheldrick, 1997) [C—H = 0.93–0.98 Å and $U_{iso}(H) = 1.2U_{eq}(C)$].

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*.

The authors are grateful to the Natural Science Foundation of Jiangsu Education Committee (grant No. 00KJB 150008) for financial support.

References

Bloxham, J., Dell, C. P. & Smith, C. W. (1994). *Heterocycles*, **38**, 399–408.
Breslow, R. & Rideout, D. C. (1980). *J. Am. Chem. Soc.* **102**, 7816–7817.
Lorente, A., Galan, C. & Fonseca, I. (1995). *Can. J. Chem.* **73**, 1546–1555.
Nawwar, G. A. M., Abdelarazck, F. M. & Swcllam, R. H. (1991). *Arch. Pharm.* **342**, 875–877.
Sharanina, L. G., Nesterov, V. N., Klokol, G. V., Rodinovskaya, L. A., Shklover, V. E., Sharanin, Yu. A., Struchkov, Yu. T. & Promonenkov, V. K. (1986). *Zh. Org. Khim.* **22**, 1315–1322.
Sheldrick, G. M. (1997). *SHELXTL*. Version 5.1. Bruker Analytical X-ray Systems, Madison, Wisconsin, USA.
Shi, D. Q., Zhang, S., Zhuang, Q. Y., Wang, X. S., Tu, S. J. & Hu, H. W. (2003). *Chin. J. Chem.* In the press.
Siemens (1994). *XSCANS*. Version 2.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Zamocka, J., Misikova, E. & Durinda, J. (1991). *Pharmatine*, **46**, 610.