

Methyl 3-amino-1-(2-chlorophenyl)-9-methoxy-5,6-dihydro-1*H*-naphtho[2,1-*b*]pyran-2-carboxylateXiang-Shan Wang,^{a,b*} Zhao-Sen Zeng,^a Yu-Ling Li,^a Da-Qing Shi,^a Xian-Yong Wei^b and Zhi-Min Zong^b^aDepartment of Chemistry, Xuzhou Normal University, Xuzhou 221116, People's Republic of China, and ^bSchool of Chemical Engineering, China University of Mining and Technology, Xuzhou 221008, People's Republic of ChinaCorrespondence e-mail:
xswang1974@yahoo.com

Key indicators

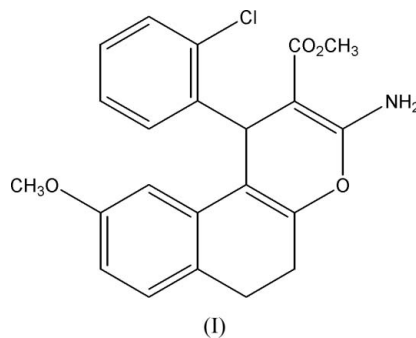
Single-crystal X-ray study
T = 273 K
Mean $\sigma(\text{C}-\text{C}) = 0.003 \text{ \AA}$
R factor = 0.040
wR factor = 0.098
Data-to-parameter ratio = 13.4For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The title compound, $\text{C}_{22}\text{H}_{20}\text{ClNO}_4$, was synthesized by the reaction of methyl 3-(2-chlorophenyl)-2-cyanoacrylate and 7-methoxy-1,2,3,4-tetrahydronaphthalen-2-one in ethanol catalyzed by KF–alumina. X-ray analysis reveals that the pyran ring adopts a half-chair conformation, while the cyclohexene ring bonded to the pyran moiety has a skew-boat form.

Received 1 March 2005
Accepted 3 March 2005
Online 11 March 2005

Comment

2-Aminochromenes are an important class of compounds, found as the main compounds in many naturally occurring products employed as cosmetics and pigments and utilized as potential biodegradable agrochemicals (Morinaka & Takahashi, 1977; Witte, *et al.*, 1986; Hafez *et al.*, 1987). The utility of fluoride salts as a potential base in a variety of synthetic reactions has been recognized in recent years. In particular, alumina coated with potassium fluoride (KF–alumina) has been reported as a useful catalyst for many reactions (Clark, 1980), resulting in higher selectivity, milder reaction conditions and easier work-up. We report here the X-ray crystal structure of the title compound, (I).



In (I), the pyran ring is slightly distorted and adopts a half-chair conformation (Fig. 1). Atom C11 deviates from the plane defined by the atoms C1/C10/C12/C13/O1 by 0.153 (2) Å. A similar distortion was observed in 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 six-membered ring C1–C4/C9/C10 adopts a skew-boat conformation. Atoms C2/C1/C10/C9 and C3/C4/C9/C10 are coplanar, respectively, and the C1–C10–C9–C4 torsion angle is $-16.9 (3)^\circ$. Atoms C1 and C2 deviate from the plane through C3/C4/C9/C10 by 0.391 (2) and 0.781 (2) Å, respectively. A similar conformation was observed in the partially saturated six-membered ring in 2-amino-4-phenyl-5,6-dihydro-benzo[*h*]quinazolin-1-one (Wang, Shi *et al.*, 2003) and 2-amino-3-cyano-4-(4-methoxy-

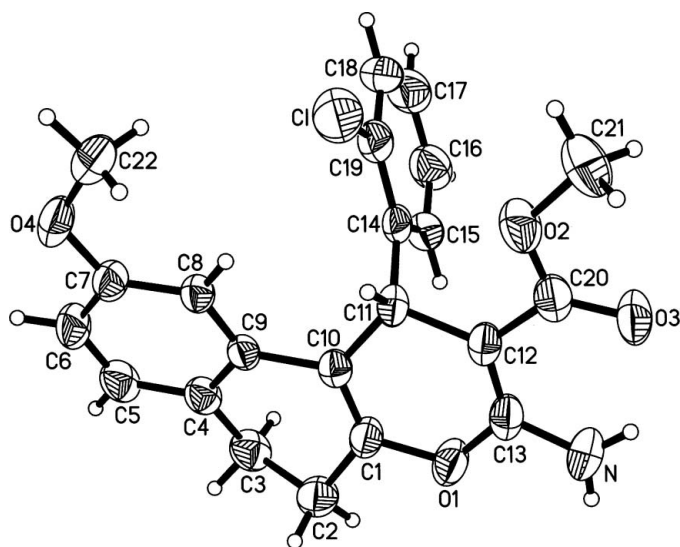


Figure 1
The molecular structure of (I), showing 30% probability displacement ellipsoids and the atom-numbering scheme.

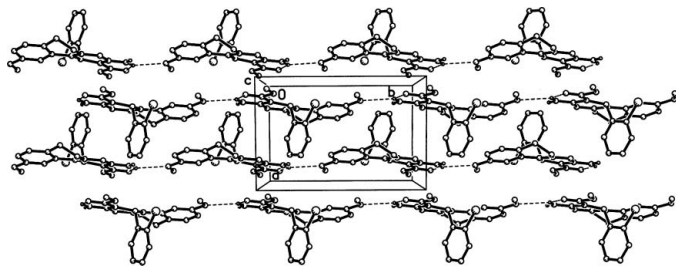


Figure 2
The molecular packing of (I). H atoms have been omitted, except for those of the amino group. Broken lines indicate hydrogen bonds.

phenyl)-1,4,5,6-tetrahydrobenzo[*h*]chromene (Wang, Li *et al.*, 2003). The 2-Cl-phenyl ring is approximately perpendicular to the tricyclic ring system.

There are intra- and intermolecular N—H...O hydrogen bonds in the crystal structure of (I) (Table 2), forming polymeric chains along the *b* axis (Fig. 2). N—H1*A* is involved in both of these interactions, while N—H1*B* does not have a hydrogen-bond acceptor.

Experimental

Compound (I) was prepared by the reaction of methyl 3-(2-chlorophenyl)-2-cyanoacrylate (0.42 g, 2 mmol) and 7-methoxy-1,2,3,4-tetrahydronaphthalene-2-one (0.35 g, 2 mmol) in the presence of KF-alumina (0.25 g) in ethanol at 293 K for 8 h (yield 78%, m.p. 448–449 K). Crystals of (I) suitable for X-ray diffraction were obtained by slow evaporation of an ethanol solution. Elemental analysis, calculated: C 66.42, H 5.07, N 3.52%; found: C 66.31, H 5.05, N 3.54%. Spectroscopic analysis: ¹H NMR (CDCl₃, δ, p.p.m.): 2.51–2.55 (*m*, 2H, CH₂), 2.76–2.81 (*m*, 2H, CH₂), 3.65 (*s*, 3H, CH₃O), 3.80 (*s*, 3H, CH₃O), 5.26 (*s*, 1H, CH), 6.20 (*s*, 2H, NH₂), 6.58 (*dd*, *J* = 8.0 Hz, *J* = 2.4 Hz, 1H, ArH), 6.94 (*d*, *J* = 8.0 Hz, 1H, ArH), 7.02 (*d*, *J* = 7.2 Hz, 1H, ArH), 7.10 (*d*, *J* = 2.4 Hz, 1H, ArH), 7.13 (*d*, *J* = 7.2 Hz, 1H, ArH), 7.22 (*d*, *J* = 7.6 Hz, 1H, ArH), 7.36 (*dd*, *J* = 7.6 Hz, *J*' = 1.6 Hz, 1H, ArH); IR (KBr, ν, cm⁻¹): 3398, 3296 (NH₂), 2942, 2837 (C—H), 1695 (C=O), 1603, 1574, 1518 (phenyl ring).

Crystal data

C₂₂H₂₀ClNO₄
M_r = 397.84
Monoclinic, *P*₂₁/*c*
a = 8.043 (1) Å
b = 11.877 (1) Å
c = 20.233 (3) Å
β = 99.40 (1)°
V = 1906.8 (4) Å³
Z = 4

*D*_x = 1.386 Mg m⁻³
Mo Kα radiation
Cell parameters from 37 reflections
θ = 3.0–13.7°
μ = 0.23 mm⁻¹
T = 273 (2) K
Block, yellow
0.52 × 0.40 × 0.40 mm

Data collection

Siemens P4 diffractometer
ω scans
Absorption correction: none
4063 measured reflections
3454 independent reflections
2135 reflections with *I* > 2σ(*I*)
*R*_{int} = 0.008

θ_{max} = 25.3°
h = 0 → 9
k = 0 → 14
l = -24 → 23
3 standard reflections
every 97 reflections
intensity decay: 2.7%

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.040
wR(*F*²) = 0.098
S = 0.87
3454 reflections
257 parameters
H-atom parameters constrained

w = 1/[σ²(*F*_o²) + (0.0525*P*)²]
where *P* = (*F*_o² + 2*F*_c²)/3
(Δ/σ)_{max} < 0.001
Δρ_{max} = 0.28 e Å⁻³
Δρ_{min} = -0.29 e Å⁻³
Extinction correction: *SHELXTL*
(Sheldrick, 1997)
Extinction coefficient: 0.0039 (6)

Table 1

Selected geometric parameters (Å, °).

O1—C13	1.355 (2)	C10—C11	1.516 (3)
O1—C1	1.392 (2)	C11—C12	1.528 (3)
C1—C10	1.328 (3)	C12—C13	1.354 (3)
C13—O1—C1	118.13 (16)	C10—C11—C12	110.36 (16)
C10—C1—O1	124.18 (19)	C13—C12—C11	121.19 (18)
C1—C10—C11	121.39 (18)	C12—C13—O1	123.65 (18)
C13—O1—C1—C10	4.7 (3)	C8—C9—C10—C1	163.24 (19)
C1—C2—C3—C4	-47.1 (2)	C4—C9—C10—C1	-16.9 (3)
C2—C3—C4—C9	36.0 (3)	C1—C10—C11—C12	-10.0 (3)
C3—C4—C9—C10	-3.1 (3)	C10—C11—C12—C13	11.2 (3)
C2—C1—C10—C9	1.2 (3)	C11—C12—C13—O1	-5.2 (3)
O1—C1—C10—C11	2.7 (3)	C1—O1—C13—C12	-3.3 (3)

Table 2

Hydrogen-bond geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N—H1 <i>A</i> ...O3	0.86	2.07	2.684 (3)	127
N—H1 <i>A</i> ...O4 ⁱ	0.86	2.56	3.007 (2)	113

Symmetry codes: (i) *x*, *y* - 1, *z*.

The H atoms were positioned geometrically and refined as riding, with C—H distances in the range 0.91–0.98 Å and N—H distances of 0.86 Å, and with *U*_{iso}(H) = 1.2*U*_{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*.

The authors thank the Natural Science Foundation (grant No. 04 KJB150139) of the Education Committee of Jiangsu Province for financial support.

References

- Clark, J. H. (1980). *Chem. Rev.* **80**, 429–452.
- Hafez, E. A., Elnagdi, M. H., Elagamey, A. A. & El-Taweel, F. A. (1987). *Heterocycles*, **26**, 903–907.
- Li, Y. L., Wang, X. S., Shi, D. Q., Tu, S. J. & Zhang, Y. (2004). *Acta Cryst.* **E60**, o1439–o1441.
- Morinaka, Y. & Takahashi, K. (1977). Jpn Pat. 52 017 498.
- Sheldrick, G. M. (1997). *SHELXTL*. Version 5.10. Bruker AXS Inc., Madison, Wisconsin, USA.
- Siemens (1994). *XSCANS*. Version 2.10. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Wang, X. S., Li, Y. L., Shi, D. Q. & Tu, S. J. (2003). *Acta Cryst.* **E59**, o1210–o1212.
- Wang, X. S., Shi, D. Q., Tu, S. J. & Yu, K. B. (2003). *Acta Cryst.* **E59**, o423–o424.
- Witte, E. C., Neuert, P. & Roesch, A. (1986). Ger. Offen. DE 3 427 985.