Acta Crystallographica Section E
Structure Reports
Online

ISSN 1600-5368

Ethyl 3-amino-1-(4-chlorophenyl)-1*H*-benzo[*f*]-chromene-2-carboxylate

Daqing Shi,[a,b]* Xiangshan Wang[a] and Qiya Zhuang[a]

[a]Department of Chemistry, Xuzhou Normal University, Xuzhou 221116, People's Republic of China, and [b]The Key Laboratory of Biotechnology for Medical Plants of Jiangsu Province, Xuzhou 221116, People's Republic of China

Correspondence e-mail: dqshi@263.net

Key indicators

Single-crystal X-ray study
T = 291 K
Mean σ(C–C) = 0.003 Å
R factor = 0.039
wR factor = 0.107
Data-to-parameter ratio = 12.7

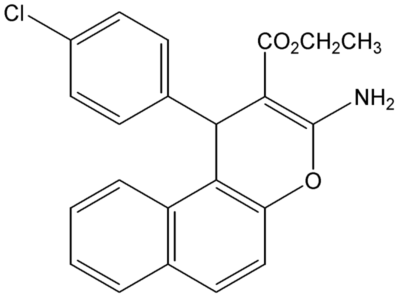
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Received 6 September 2004
Accepted 13 September 2004
Online 18 September 2004

The title compound, $C_{22}H_{18}ClNO_3$, was synthesized by the reaction of 2-naphthol with ethyl 2-cyano-3-(4-chlorophenyl)-acrylate in the presence of triethylbenzylammonium chloride in water. X-ray analysis reveals that the pyran ring adopts a boat conformation.

Comment

4*H*-Chromene is a construction unit of some natural products. 4*H*-Chromenes with amino and cyano groups are also the synthons of some special natural products (Hatokeyama *et al.*, 1998; O'Callaghan & McMurry, 1995). We have reported the synthesis of some 4*H*-chromene derivatives (Shi *et al.*, 2002; Zhuang *et al.*, 2002). As part of our program aimed at developing new and environmentally friendly methodologies for the preparation of fine chemicals (Shi *et al.*, 2003), we have synthesized the title compound, (I), in water and report here its X-ray crystal structure.



(I)

The title compound is shown in Fig. 1. The bond lengths and angles in (I) have normal values (Table 1). The pyran ring adopts a boat conformation: atoms C15, C16, C18 and C19 form the least-squares plane, while atoms O1 and C17 deviate from this plane by 0.137 (2) and 0.292 (2) Å, respectively. A similar conformation was observed in the structure of 2-amino-4-(2-chlorophenyl)-3-ethoxycarbonyl-4*H*-benzo[*f*]-chromene (Zhuang *et al.*, 2003). The naphthalene ring system is essentially planar. The naphthalene and the substituted phenyl ring planes form dihedral angles of 6.94 (2) and 88.86 (3)°, respectively, with the C15/C16/C18/C19 plane. In addition, because of the existence of a conjugated system, the C19—N bond length of 1.350 (2) Å is shorter than the typical Csp^2—N bond distance (Lorente *et al.*, 1995). The sum of the bond angles [351.8°] around the N atom indicates a slightly pyramidal geometry. An intramolecular hydrogen bond is formed between the amine group and atom O3 of the carbonyl group (see Table 2).

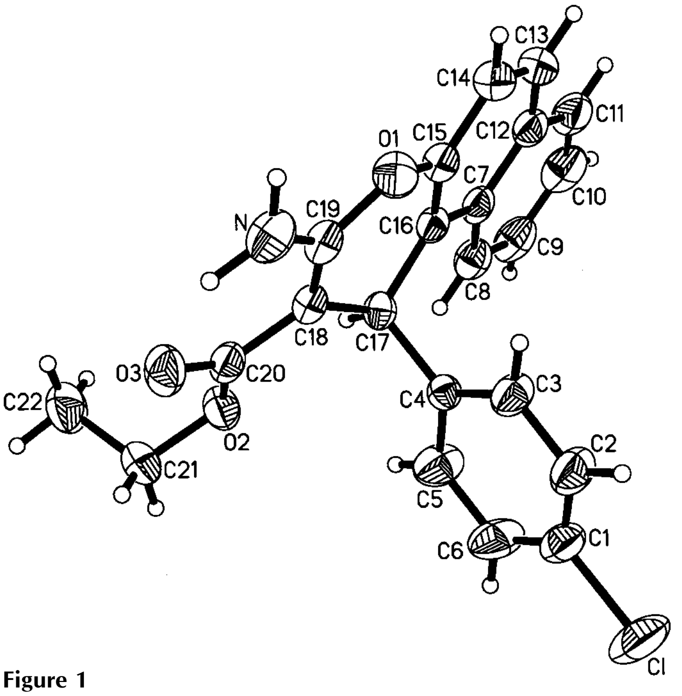


Figure 1
The molecular structure of (I), showing 50% probability displacement ellipsoids and the atom-numbering scheme.

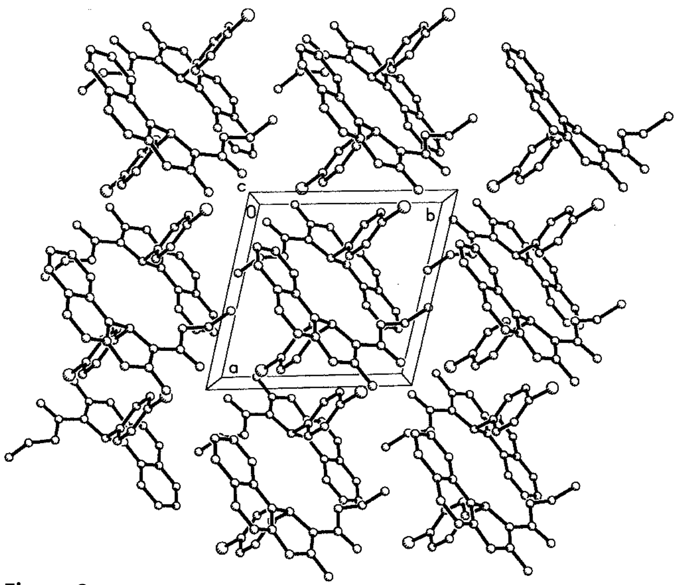


Figure 2
The molecular packing in the crystal structure of (I).

Experimental

The title compound, (I), was prepared by the reaction of 2-naphthol (0.72 g, 5 mmol) with ethyl 2-cyano-3-(4-chlorophenyl)acrylate (1.18 g, 5 mmol) in the presence of triethylbenzylammonium chloride (0.2 g) in water (10 ml) at 363 K for 14 h (yield 91%, m.p. 463–465 K). IR: 3475, 3325 (NH_2), 1675 (CO), 1630, 1505, 1480, 825 (phenyl ring); ^{1}H NMR; 1.26 (3H, *t*, $J = 7.2$ Hz, CH_3), 4.09 (2H, *q*, $J = 7.2$ Hz, OCH_2), 5.51 (1H, *s*, CH), 7.23–7.53 (7H, *m*, ArH), 7.65 (2H, *s*, NH_2), 7.92 (2H, *d*, $J = 8.0$ Hz, ArH), 7.99 (1H, *d*, $J = 8.0$ Hz, ArH). Analysis calculated for $C_{22}H_{18}ClNO_3$: C 69.57, H 4.78, N 3.69%; found: C 69.46, H 4.98, N 3.80%. Single crystals suitable for X-ray diffraction were obtained by slow evaporation of an *N*,*N*-dimethylformamide–water solution.

Crystal data

$C_{22}H_{18}ClNO_3$
$M_r = 379.82$
Triclinic, $P\overline{1}$
$a = 9.292$ (1) Å
$b = 9.449$ (1) Å
$c = 10.973$ (1) Å
$\alpha = 94.99$ (1)°
$\beta = 98.14$ (2)°
$\gamma = 102.84$ (1)°
$V = 922.85$ (18) Å^3
$Z = 2$
$D_x = 1.367$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 2.7$–12.7°
$\mu = 0.23$ mm^{-1}
$T = 291$ (2) K
Block, colorless
0.54 × 0.50 × 0.32 mm

Data collection

Siemens *P*4 diffractometer
ω scans
Absorption correction: ψ scans (*XSCANS*; Siemens, 1994)
$T_{min} = 0.852$, $T_{max} = 0.929$
3558 measured reflections
3229 independent reflections
2323 reflections with $I > 2\sigma(I)$
$R_{int} = 0.010$
$\theta_{max} = 25.0°$
$h = 0 \rightarrow 11$
$k = -11 \rightarrow 10$
$l = -13 \rightarrow 12$
3 standard reflections every 97 reflections intensity decay: 3.6%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.039$
$wR(F^2) = 0.107$
$S = 1.06$
3229 reflections
254 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.054P)^2 + 0.0607P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.23$ e Å^{-3}
$\Delta\rho_{min} = -0.24$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.025 (3)

Table 1
Selected geometric parameters (Å, °).

O1—C19	1.358 (2)	N—C19	1.350 (2)
O1—C15	1.394 (2)	C15—C16	1.363 (2)
O2—C20	1.349 (2)	C16—C17	1.502 (2)
O2—C21	1.452 (2)	C17—C18	1.514 (2)
O3—C20	1.227 (2)		
C19—O1—C15	118.58 (14)	C19—C18—C17	120.20 (16)
C20—O2—C21	116.71 (15)	C20—C18—C17	120.77 (16)
C16—C15—O1	122.16 (16)	N—C19—C18	126.8 (2)
O1—C15—C14	114.03 (17)	N—C19—O1	110.69 (18)
C15—C16—C17	120.03 (15)	C18—C19—O1	122.53 (16)
C16—C17—C18	110.48 (14)	O3—C20—O2	121.29 (17)
C16—C17—C4	111.09 (13)	O3—C20—C18	126.09 (18)
C18—C17—C4	110.76 (13)	O2—C20—C18	112.62 (15)
C19—C18—C20	119.02 (16)		
C19—O1—C15—C16	−15.3 (2)	C20—C18—C19—O1	−171.58 (15)
C19—O1—C15—C14	166.09 (15)	C17—C18—C19—O1	9.7 (3)
C4—C17—C18—C19	98.60 (18)	C15—O1—C19—N	−169.63 (14)
C4—C17—C18—C20	−80.12 (19)	C15—O1—C19—C18	11.5 (2)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N—H1*A*···O3	1.01 (3)	1.89 (3)	2.690 (3)	133 (2)

Amino atoms H1*A* and H1*B* were refined isotropically. The positions of the other H atoms were calculated and refined as riding, with 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*.

We thank the foundation of the 'Surpassing Project' of Jiangsu Province for financial support.

References

Hatokeyama, S., Ochi, N., Numata, H. & Takano, S. (1998). *J. Chem. Soc. Chem. Commun.* pp. 1202–1204.

Lorente, A., Galan, C., Fonseca, I. & Sanz-Aparicio, J. (1995). *Can. J. Chem.* **73**, 1546–1555.

O'Callaghan, C. N. & McMurry, T. B. H. (1995). *J. Chem. Res.* (*S*), p. 214.

Sheldrick, G. M. (1997). *SHELXTL*. Version 5.1. Bruker AXS Inc., Madison, Wisconsin, USA.

Shi, D. Q., Chen, J., Zhuang, Q. Y. & Hu, H. W. (2003). *J. Chem. Res.* (*S*), pp. 674–675.

Shi, D. Q., Wang, X. S. & Tu, S. J. (2002). *Chin. J. Org. Chem.* **22**, 1053–1056.

Siemens (1994). *XSCANS*. Version 2.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Zhuang, Q. Y., Shi, D. Q., Tu, S. J. & Wang, X. S. (2002). *Chin. J. Appl. Chem.* **19**, 1019–1020.

Zhuang, Q. Y., Shi, D. Q. & Wang, X. S.(2003). *Acta Cryst.* E**59**, o1474–o1475.