

Ethyl 2-amino-4-(2,4-dichlorophenyl)-4H-benzo[f]chromene-3-carboxylate

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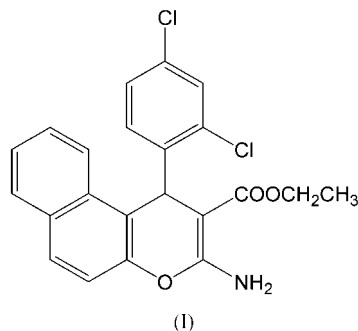
Key indicators

Single-crystal X-ray study
T = 292 K
Mean $\sigma(\text{C}-\text{C}) = 0.004 \text{ \AA}$
R factor = 0.044
wR factor = 0.127
Data-to-parameter ratio = 12.8For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The title compound, $\text{C}_{22}\text{H}_{17}\text{Cl}_2\text{NO}_3$, was synthesized by the reaction of 2-naphthol with 2,4-dichlorobenzaldehyde and ethyl cyanoacetate in ethanol in the presence of $\text{KF}/\text{Al}_2\text{O}_3$ as catalyst. X-ray analysis reveals that the pyran ring adopts a boat conformation. In the crystal structure, the amino group is involved in both intra- and intermolecular $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds.

Comment

4H-Chromene is a building unit of some natural products. 4H-Chromenes with amino and cyano groups are also synthons of some special natural products (Hatokeyama *et al.*, 1988; O'Callaghan & McMurry, 1995). We have previously reported the synthesis of some 4H-chromene derivatives (Shi *et al.*, 2002; Zhuang *et al.*, 2002). We report here the X-ray crystal structure of the title compound, (I).



The bond lengths and angles in (I) show normal values (Table 1). The pyran ring adopts a boat conformation, with atoms O1 and C3 deviating from the C1/C2/C4/C5 plane by 0.194 (2) and 0.301 (1) Å, respectively. A similar distortion was observed in the structure of 2-amino-4-(2-chlorophenyl)-3-ethoxycarbonyl-4H-benzo[f]chromene (Zhuang *et al.*, 2003). The naphthalene and substituted phenyl ring planes form dihedral angles of 10.02 (3) and 91.92 (2)°, respectively, with the C1/C2/C4/C5 plane. An intramolecular hydrogen bond is formed between the amino group and atom O3 of the carbonyl group. Molecules related by 2_1 screw axes are linked by intermolecular $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds, forming chains in the *b* axis direction (Fig. 2 and Table 2)

Experimental

The title compound (I), was prepared by the reaction of 2-naphthol with 2,4-dichlorobenzaldehyde and ethyl cyanoacetate in ethanol in the presence of $\text{KF}/\text{Al}_2\text{O}_3$ as catalyst (m.p. 468–470 K). Single crystals suitable for X-ray diffraction analysis were obtained by slow evaporation of an *N,N*-dimethylformamide–water solution.

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Crystal data

$C_{22}H_{17}Cl_2NO_3$
 $M_r = 414.27$
 Monoclinic, $P2_1/n$
 $a = 14.505$ (2) Å
 $b = 9.037$ (1) Å
 $c = 14.913$ (2) Å
 $\beta = 101.21$ (1)°
 $V = 1917.5$ (4) Å³
 $Z = 4$

$D_x = 1.435$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 27 reflections
 $\theta = 2.9$ – 15.2°
 $\mu = 0.36$ mm⁻¹
 $T = 292$ (2) K
 Block, colorless
 $0.56 \times 0.52 \times 0.24$ mm

Data collection

Siemens P4 diffractometer
 ω scans
 Absorption correction: ψ scan
 (XSCANS; Siemens, 1994)
 $T_{\min} = 0.770$, $T_{\max} = 0.917$
 4195 measured reflections
 3379 independent reflections
 2292 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.013$
 $\theta_{\text{max}} = 25.0^\circ$
 $h = -10 \rightarrow 17$
 $k = -5 \rightarrow 10$
 $l = -17 \rightarrow 17$
 3 standard reflections
 every 97 reflections
 intensity decay: 2.7%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.044$
 $wR(F^2) = 0.127$
 $S = 1.09$
 3379 reflections
 263 parameters
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0657P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.43$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.26$ e Å⁻³
 Extinction correction: *SHELXL97*
 Extinction coefficient: 0.0052 (13)

Table 1

Selected geometric parameters (Å, °).

O1–C1	1.361 (3)	N–C1	1.335 (3)
O1–C5	1.391 (3)	C1–C2	1.362 (3)
O2–C14	1.343 (3)	C2–C3	1.520 (3)
O2–C15	1.452 (3)	C3–C4	1.513 (3)
O3–C14	1.233 (3)	C4–C5	1.365 (3)
C1–O1–C5	117.88 (19)	C1–C2–C3	120.4 (2)
C14–O2–C15	118.6 (2)	O1–C5–C6	114.0 (2)
N–C1–O1	109.7 (2)	O3–C14–O2	121.6 (2)
N–C1–C2	128.1 (3)	O3–C14–C2	126.8 (2)
O1–C1–C2	122.2 (2)	O2–C14–C2	111.6 (2)
C1–C2–C14	119.2 (2)	O2–C15–C16	107.7 (3)
C5–O1–C1–N	–165.7 (2)	C1–O1–C5–C4	–21.6 (3)
C5–O1–C1–C2	16.0 (3)	C1–O1–C5–C6	158.7 (2)
N–C1–C2–C14	6.6 (4)	O1–C5–C6–C7	178.1 (2)
O1–C1–C2–C14	–175.5 (2)	C15–O2–C14–O3	–11.5 (4)
N–C1–C2–C3	–168.9 (2)	C15–O2–C14–C2	170.0 (3)
O1–C1–C2–C3	9.1 (4)	C14–O2–C15–C16	–87.6 (4)

Table 2

Hydrogen-bonding geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N–H1A \cdots O3	0.859 (10)	2.09 (2)	2.726 (3)	130 (2)
N–H1B \cdots O3 ⁱ	0.851 (10)	2.215 (13)	3.033 (3)	161 (3)

 Symmetry code: (i) $\frac{3}{2} - x, y - \frac{1}{2}, \frac{3}{2} - z$.

Amino atoms H1A and H1B 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 $U_{\text{iso}}(H) = 1.2U_{\text{eq}}(C)$.

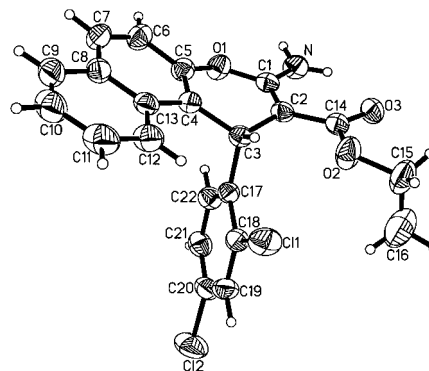


Figure 1

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

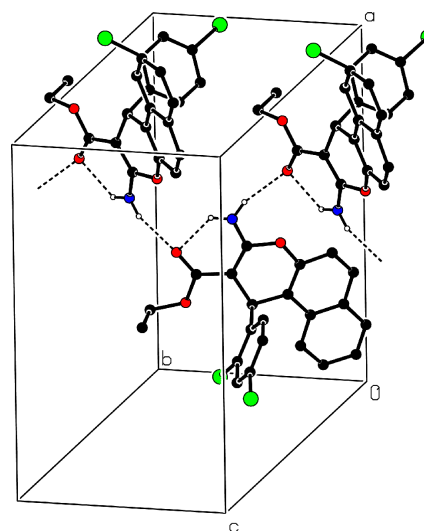


Figure 2

View (Spek, 2003) of part of the crystal structure of (I), showing hydrogen bonding as dashed lines. Colour codes: green Cl, red O, blue N, and black 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*.

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