

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

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Key indicators

Single-crystal X-ray study

$T = 292\text{ K}$

Mean $\sigma(\text{C}-\text{C}) = 0.003\text{ \AA}$

R factor = 0.041

wR factor = 0.117

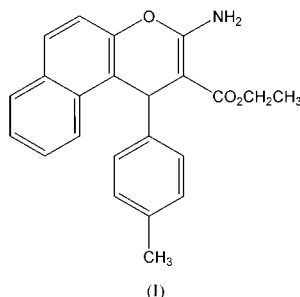
Data-to-parameter ratio = 12.8

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

The pyran ring of the title molecule, $\text{C}_{23}\text{H}_{21}\text{NO}_3$, adopts a flattened 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. The molecules form centrosymmetric dimers which are interlinked by weak $\text{C}-\text{H}\cdots\pi$ interactions.

Comment

4*H*-Chromene is a structural 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 previously reported the synthesis of some 4*H*-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). In the title molecule, the naphthalene ring system is planar within 0.014 (3)\ \AA . The pyran ring adopts a flattened boat conformation, with atoms O1 and C3 deviating from the C1/C2/C4/C5 plane by 0.143 (1) and 0.299 (2)\ \AA , respectively. The naphthalene and substituted phenyl ring planes form dihedral angles of 7.60 (5) and 89.16 (6)° , respectively, with the C1/C2/C4/C5 plane. The sum of the bond angles [353.0 (2)°] around N indicates a planar geometry. An intramolecular $\text{N}-\text{H1A}\cdots\text{O3}$ hydrogen bond is formed between the amino N atom and O atom of the carbonyl group (Table 2). The other H atom of the amino group is involved in weak $\text{N}-\text{H1B}\cdots\text{O3}(-x, -y, 1-z)$ interactions to form centrosymmetric dimers (Fig. 2). The dimers are interlinked by weak $\text{C}-\text{H}\cdots\pi$ interactions involving the symmetry-related substituted phenyl rings.

Experimental

The title compound was prepared by the reaction of 2-naphthol with 4-methylbenzaldehyde and ethyl cyanoacetate in ethanol, in the presence of piperidine as catalyst. Single crystals suitable for X-ray diffraction were obtained by slow evaporation of an *N,N*-dimethylformamide–water solution.

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Crystal data

$C_{23}H_{21}NO_3$
 $M_r = 359.41$
 Triclinic, $P\bar{1}$
 $a = 9.394$ (2) Å
 $b = 9.396$ (1) Å
 $c = 11.005$ (2) Å
 $\alpha = 94.98$ (1)°
 $\beta = 98.30$ (1)°
 $\gamma = 102.95$ (1)°
 $V = 929.6$ (3) Å³

$Z = 2$
 $D_x = 1.284$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 31 reflections
 $\theta = 3.7$ – 14.3 °
 $\mu = 0.09$ mm⁻¹
 $T = 292$ (2) K
 Block, colorless
 $0.56 \times 0.50 \times 0.36$ mm

Data collection

Siemens $P4$ diffractometer
 ω scans
 Absorption correction: none
 3602 measured reflections
 3264 independent reflections
 2205 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.012$

$\theta_{max} = 25.0$ °
 $h = 0 \rightarrow 11$
 $k = -11 \rightarrow 10$
 $l = -13 \rightarrow 12$
 3 standard reflections every 97 reflections
 intensity decay: 3.0%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.041$
 $wR(F^2) = 0.117$
 $S = 1.01$
 3264 reflections
 255 parameters
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.064P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} < 0.001$
 $\Delta\rho_{max} = 0.16$ e Å⁻³
 $\Delta\rho_{min} = -0.15$ e Å⁻³
 Extinction correction: *SHELXTL*
 Extinction coefficient: 0.029 (4)

Table 1

Selected geometric parameters (Å, °).

O1—C1	1.353 (2)	N—C1	1.352 (2)
O1—C5	1.399 (2)	C1—C2	1.356 (2)
O2—C14	1.347 (2)	C2—C3	1.513 (2)
O2—C15	1.454 (2)	C3—C4	1.508 (2)
O3—C14	1.2305 (19)		
N—C1—O1	110.26 (17)	C4—C3—C17	111.12 (12)
N—C1—C2	126.81 (19)	C2—C3—C17	110.72 (13)
C4—C3—C2	110.25 (13)	O3—C14—C2	126.33 (18)
C14—C2—C3—C17	-80.72 (18)	C1—C2—C14—O3	-5.4 (3)
C17—C3—C4—C13	75.62 (18)	C3—C2—C14—O2	-7.6 (2)
C15—O2—C14—O3	3.0 (2)		

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	0.88 (1)	1.98 (2)	2.697 (3)	137 (2)
N—H1B \cdots O3 ⁱ	0.86 (1)	2.54 (2)	2.969 (2)	112 (1)
C16—H16B \cdots CgP ⁱⁱ	0.96	3.01	3.785 (2)	138
C23—H23C \cdots CgP ⁱⁱⁱ	0.96	2.98	3.789 (2)	143

Symmetry codes: (i) $-x, -y, 1-z$; (ii) $x, y-1, z$; (iii) $-x, 1-y, 2-z$. CgP denotes the centroid of the substituted phenyl ring.

The C-bound H atoms were positioned geometrically and were treated as riding on their parent C atoms, with C—H distances in the range 0.93–0.97 Å; the $U_{iso}(H)$ values were set equal to $1.5U_{eq}(C)$ for the methyl H atoms and $1.2U_{eq}(C)$ for the aromatic and methylene H

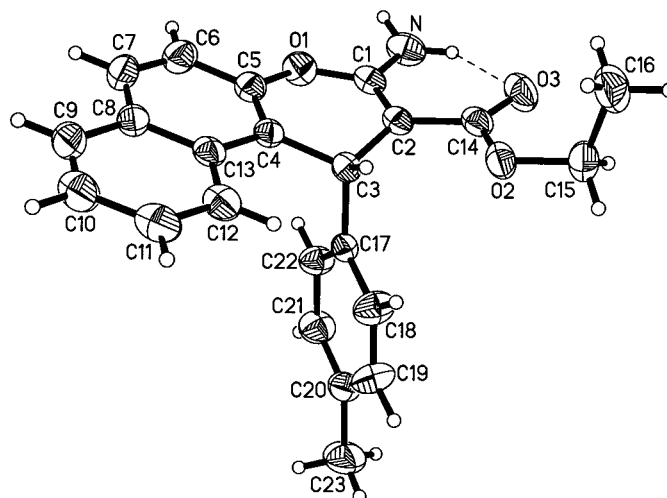


Figure 1

The structure of the title compound, showing 50% probability displacement ellipsoids and the atom-numbering scheme.

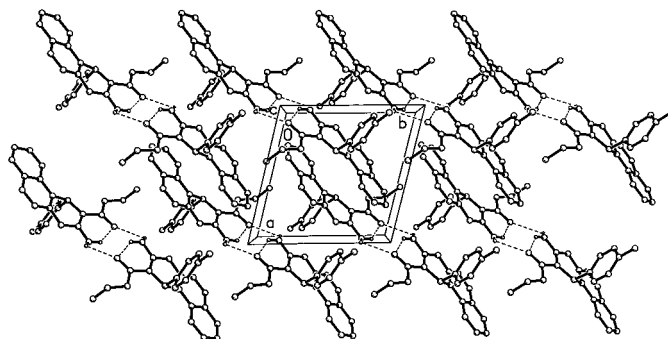


Figure 2

A view of the molecular packing down the c axis.

atoms. The amino H atoms, H1A and H1B, were located from a difference Fourier map and their positional and isotropic displacement parameters were refined with N—H distances restrained to be 0.86 (1) Å.

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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References

- Hatokeyama, S., Ochi, N., Numata, H. & Takano, S. (1998). *J. Chem. Soc. Chem. Commun.* **17**, 1202–1204.
 O’Callaghan, C. N. & McMurry, T. B. H. (1995). *J. Chem. Res. (S)*, pp. 214–215.
 Sheldrick, G. M. (1997). *SHELXTL*. Version 5.1. Bruker AXS Inc., Madison, Wisconsin, USA.
 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.