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Ethyl 9-amino-7-(4-methoxyphenyl)-7*H*-pyrano[3,2-*c*]coumarin-8-carboxylate

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Key indicators

Single-crystal X-ray study
T = 273 K
Mean σ(C–C) = 0.002 Å
R factor = 0.037
wR factor = 0.095
Data-to-parameter ratio = 13.6

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

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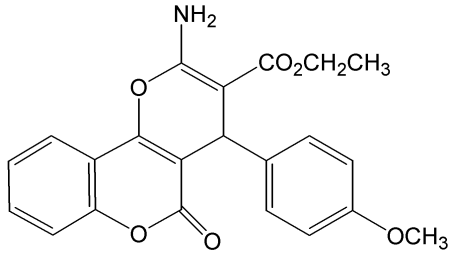
The title compound, $C_{22}H_{19}NO_6$, was synthesized by the reaction of 4-hydroxycoumarin and ethyl 4′-methoxy-2-cyanocinnamate in the presence of triethylbenzylammonium chloride in an aqueous medium. In the crystal structure, the amino group is involved in both intra- and intermolecular N—H···O hydrogen bonds.

Comment

Coumarin and its derivatives are natural compounds and are important chemicals in the perfume, cosmetic and pharmaceutical industries (Soine, 1964). As part of our program aimed at developing new and environmentally friendly methodologies for the preparation of fine chemicals (Shi, Chen *et al.*, 2003), we have synthesized 7*H*-pyrano[3,2-*c*]-coumarin derivatives by a two-component reaction employing water as the reaction medium. We report here the crystal structure of the title compound, (I).



(I)

In (I), the pyran ring of coumarin is almost planar, with deviations of 0.013 (2), 0.028 (2), −0.032 (2), −0.048 (3), 0.44 (2) and −0.005 (2) Å for atoms C1, C2, C7, C9, C8 and O2, respectively (Fig. 1 and Table 1). The other pyran ring adopts a flattened boat conformation: atoms O1 and C10 deviate from the plane defined by atoms C1/C9/C11/C12 by 0.118 (2) and 0.261 (2) Å, respectively. A similar distortion was observed in ethyl 2-amino-4-(2,4-dichlorophenyl)-4*H*-benzo[*f*]chromene-3-carboxylate (Shi, Wang *et al.*, 2003). The pyran ring of coumarin and the substituted phenyl ring make dihedral angles of 3.4 (2) and 90.4 (2)°, respectively. The sum of the bond angles around N (358.6°) indicates a planar geometry.

An intramolecular hydrogen bond is formed between the amino N and carbonyl O6 atoms (Table 2). The other H atom of the amino group is involved in N—H1*A*···O3 ($x+1, y, z$) interactions to form columns along the *a* axis (Fig. 2).

Experimental

The title compound, (I), was prepared by the reaction of 4-hydroxycoumarin (0.32 g) and ethyl 4′-methoxy-2-cyanocinnamate (0.46 g) in the presence of triethylbenzylammonium chloride (0.1 g) in water at 348 K for 8 h (yield 89%; m.p. 433–435 K). Single crystals of (I) suitable for X-ray diffraction were obtained by slow evaporation of an *N*,*N*-dimethylformamide–water solution.

Crystal data

$C_{22}H_{19}NO_6$
M_r = 393.38
Triclinic, $P\overline{1}$
a = 7.649 (1) Å
b = 9.332 (1) Å
c = 14.725 (2) Å
α = 74.34 (1)°
β = 75.77 (1)°
γ = 71.16 (1)°
V = 943.2 (3) Å^3
Z = 2
D_x = 1.385 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 37 reflections
θ = 3.0–15.8°
μ = 0.10 mm^{-1}
T = 273 (2) K
Block, colourless
0.56 × 0.30 × 0.20 mm

Data collection

Siemens *P*4 diffractometer
ω scans
Absorption correction: none
4244 measured reflections
3710 independent reflections
2473 reflections with $I > 2\sigma(I)$
R_{int} = 0.008
θ_{max} = 26.0°
$h = 0 \rightarrow 9$
$k = -10 \rightarrow 11$
$l = -17 \rightarrow 18$
3 standard reflections
every 97 reflections
intensity decay: 3.1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.037
$wR(F^2)$ = 0.095
S = 0.95
3710 reflections
273 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0488P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.18 e Å^{-3}
$\Delta\rho_{min}$ = −0.16 e Å^{-3}
Extinction correction: *SHELXTL*
Extinction coefficient: 0.060 (3)

Table 1
Selected geometric parameters (Å, °).

O1—C1	1.3656 (17)	O6—C20	1.2213 (17)
O1—C12	1.3797 (16)	C1—C9	1.3411 (19)
O2—C7	1.3831 (18)	C1—C2	1.4416 (19)
O2—C8	1.3852 (18)	C2—C7	1.389 (2)
O3—C8	1.2065 (17)	C8—C9	1.439 (2)
O4—C16	1.3724 (18)	C9—C10	1.5108 (19)
O4—C19	1.426 (2)	C10—C11	1.514 (2)
O5—C20	1.3481 (18)	C11—C12	1.355 (2)
O5—C21	1.4443 (18)		
C12—O1—C1—C9	−11.3 (2)	C7—O2—C8—C9	−5.27 (19)
C12—O1—C1—C2	170.60 (12)	C2—C1—C9—C8	−6.6 (2)
C9—C1—C2—C7	−0.3 (2)	O1—C1—C9—C10	−6.2 (2)
C8—O2—C7—C2	−1.8 (2)	O2—C8—C9—C1	9.4 (2)
C1—C2—C7—O2	4.7 (2)	C1—C9—C10—C11	20.65 (18)

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

D—H···A	D—H	H···A	D···A	D—H···A
N—H1B···O6	0.872 (9)	2.099 (16)	2.7194 (19)	127.5 (15)
N—H1A···O3^{i}	0.865 (9)	2.267 (12)	3.067 (2)	153.9 (16)

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

Amino atoms H1*A* and H1*B* were located in difference density maps and refined isotropically. The positions of the other H atoms were calculated and refined as riding, with C—H = 0.91–0.98 Å and U_{iso}(H) = 1.2U_{eq}(C).

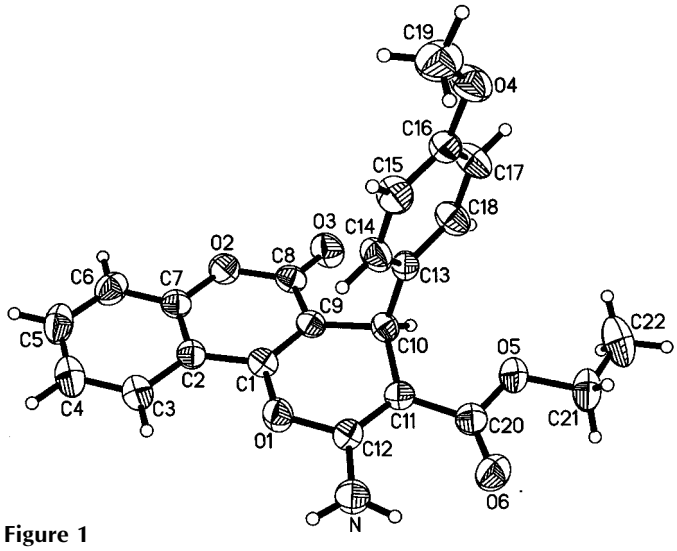


Figure 1
The molecular structure of (I), showing 30% probability displacement ellipsoids and the atom-numbering scheme.

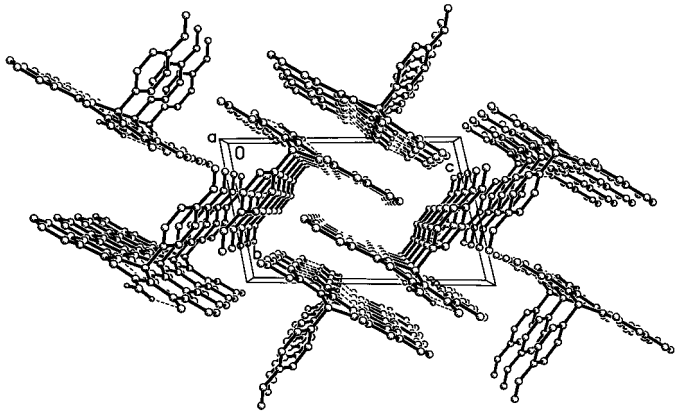


Figure 2
View of the crystal structure of (I) along the *a* axis. Dashed lines indicate hydrogen bonds.

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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