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Ethyl 2-amino-5-oxo-4-(*p*-tolyl)-4*H*,5*H*-pyrano[3,2-*c*]chromene-8-carboxylate

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Key indicators

Single-crystal X-ray study
T = 296 K
Mean σ(C–C) = 0.003 Å
Disorder in main residue
R factor = 0.040
wR factor = 0.101
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.

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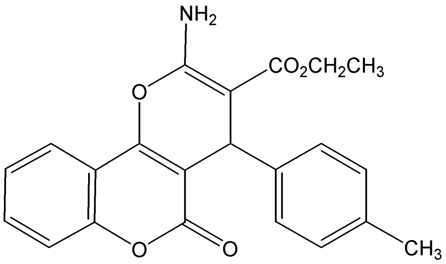
The title compound, $C_{22}H_{19}NO_5$, was synthesized by the reaction of 4-hydroxycoumarin and ethyl 4′-methyl-2-cyano-cinnamate in the presence of triethylbenzylammonium chloride in an aqueous medium. In the crystal structure, the amino group is involved in both intra- and intermolecular N—H···O hydrogen 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; Shi, Wu *et al.*, 2003) we have synthesized 4*H*-pyrano[3,2-*c*]chromenone derivatives by a two-component reaction employing water as the reaction medium. We report here the crystal structure of the title compound, (I), synthesized by the reation of 4-hydroxycoumarin and ethyl 4′-methyl-2-cyanocinnamate in the presence of triethylbenzylammonium chloride in an aqueous medium.



(I)

In (I), (Fig. 1) the pyran ring of coumarin is almost planar, with deviations of −0.005 (2), 0.009 (2), −0.010 (2), 0.017 (2), −0.007 (2) and −0.013 (2) Å for atoms C1, C2, C7, C8, C9 and O2, respectively. The other pyran ring adopts a flattened boat conformation; atoms O1 and C10 deviate from the plane defined by atoms C1, C9, C11 and C12 by 0.164 (2) and 0.331 (3) Å, respectively. Similar distortions were observed in the structure of ethyl 2-amino-4-(2,4-dichlorophenyl)-4*H*-benzo[*f*]chromene-3-carboxylate (Shi, Wang *et al.*, 2003) and ethyl 9-amino-7-(4-methoxyphenyl)-7*H*-pyrano[3,2-*c*]-coumarin-8-carboxylate (Wang *et al.*, 2004). The dihedral angle between the coumarin pyran ring O2, C7, C2, C1, C9, C8 and the fused benzene ring is 0.5 (2)° and that between the coumarin pyran ring and the *p*-tolyl ring is 81.8 (2)°. The sum of the bond angles around N (356.6°) indicates a planar

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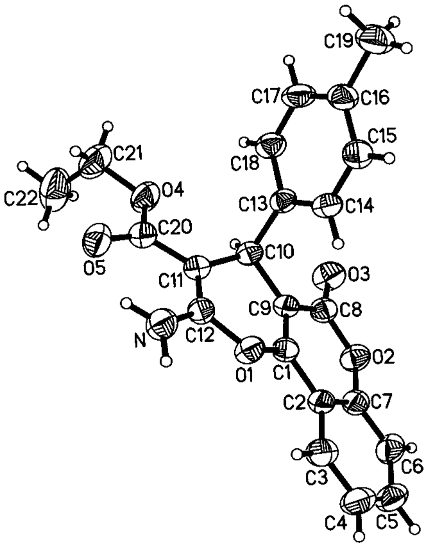

Figure 1
The molecular structure of (I), showing 30% probability displacement ellipsoids and the atom-numbering scheme. Only one of the disorder components is shown.

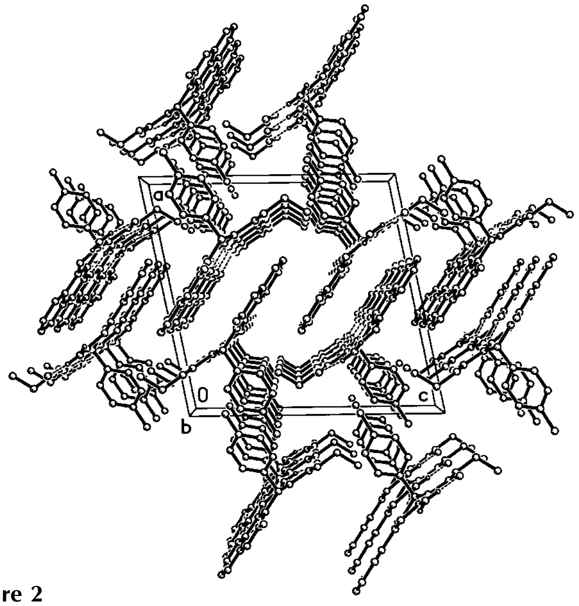

Figure 2
A molecular packing diagram of the crystal structure of (I). Dashed lines indicate hydrogen bonds. H atoms have been omitted.

geometry. The bond lengths and angles in (I) (Table 1) have normal values.

An intramolecular hydrogen bond is formed between the amino N atom and atom O5 of the carbonyl group (Table 2). The other H atom of the amino group is involved in N—H1B···O3(x, $y-1$, z) interactions, forming polymeric chains (Fig. 2).

Experimental

The title compound was prepared by the reaction of 4-hydroxycoumarin (0.32 g) and ethyl 4′-methyl-2-cyanocinnamate (0.43 g) in the presence of triethylbenzylammonium chloride (0.1 g) in water at 348 K for 6 h (yield 80%, m.p. 464–465 K). IR: 3395, 3284 (NH_2), 1710, 1683 (C=O), 1611, 1532, 1492, 1456, 786, 762, 750 (benzene ring); ^{1}H NMR: 1.12 (3H, *t*, *J* = 7.2 Hz, CH_3), 2.21 (3H, *s*, CH_3), 3.99 (2H, *q*, *J* = 7.2 Hz, CH_2O), 4.66 (1H, *s*, CH), 7.03 (2H, *d*, *J* = 8.0 Hz, ArH), 7.11 (2H, *d*, *J* = 8.0 Hz, ArH), 7.43–7.51 (2H, *m*, ArH), 7.68–7.71 (1H, *m*, ArH), 7.80 (2H, *s*, NH_2), 7.97 (1H, *d*, *J* = 7.2 Hz, ArH); Analysis calculated for $C_{22}H_{19}NO_5$: C 70,02; H 5.07; N 3.71%; found: C 70.26; H 4.83, N 3.69%. Single crystals suitable for X-ray diffraction were obtained by slow evaporation of an *N*,*N*-dimethylformamide–water solution.

Crystal data

$C_{22}H_{19}NO_5$
$M_r = 377.38$
Monoclinic, $P2_1/c$
$a = 15.239$ (2) Å
$b = 7.850$ (1) Å
$c = 15.846$ (3) Å
$\beta = 101.00$ (1)°
$V = 1860.7$ (5) Å^3
$Z = 4$

$D_x = 1.347$ Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 39 reflections
$\theta = 3.1$–$14.8°$
$\mu = 0.10$ mm^{-1}
$T = 296$ (2) K
Block, colorless
0.58 × 0.52 × 0.12 mm

Data collection

Siemens *P*4 diffractometer
ω scans
Absorption correction: none
3918 measured reflections
3379 independent reflections
2173 reflections with $I > 2\sigma(I)$
$R_{int} = 0.014$

$\theta_{max} = 25.3°$
$h = 0 \rightarrow 18$
$k = 0 \rightarrow 9$
$l = -19 \rightarrow 18$
3 standard reflections every 97 reflections intensity decay: 4.9%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.040$
$wR(F^2) = 0.101$
$S = 0.91$
3379 reflections
263 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0538P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.17$ e Å^{-3}
$\Delta\rho_{min} = -0.15$ e Å^{-3}
Extinction correction: *SHELXL*
Extinction coefficient: 0.0124 (9)

Table 1
Selected geometric parameters (Å, °).

O1—C1	1.365 (2)	N—C12	1.330 (2)
O1—C12	1.381 (2)	C1—C9	1.339 (2)
O2—C8	1.379 (2)	C1—C2	1.437 (2)
O2—C7	1.382 (2)	C8—C9	1.447 (2)
O3—C8	1.207 (2)	C9—C10	1.509 (2)
O4—C20	1.349 (2)	C10—C11	1.521 (2)
O4—C21	1.449 (2)	C11—C12	1.364 (2)
O5—C20	1.224 (2)		
C1—O1—C12	117.65 (13)	O3—C8—C9	125.82 (16)
C8—O2—C7	121.75 (14)	O2—C8—C9	118.19 (16)
C20—O4—C21	117.13 (16)	C1—C9—C8	118.84 (16)
C9—C1—O1	122.75 (15)	C1—C9—C10	121.54 (15)
C9—C1—C2	123.37 (16)	C8—C9—C10	119.60 (15)
O1—C1—C2	113.88 (15)	C9—C10—C11	108.14 (13)
O2—C7—C2	121.38 (15)	N—C12—C11	128.99 (17)
O2—C7—C6	116.85 (17)	N—C12—O1	109.15 (16)
O3—C8—O2	115.99 (16)	C11—C12—O1	121.84 (16)
C12—O1—C1—C9	19.3 (2)	C9—C10—C11—C12	28.4 (2)
C12—O1—C1—C2	−161.54 (14)	C9—C10—C11—C20	−157.01 (15)
C8—O2—C7—C2	1.7 (2)	C20—C11—C12—N	−8.7 (3)
C7—O2—C8—O3	176.84 (15)	C10—C11—C12—N	166.09 (18)
C7—O2—C8—C9	−3.2 (2)	C20—C11—C12—O1	172.70 (15)
O1—C1—C9—C8	178.61 (15)	C10—C11—C12—O1	−12.5 (2)
C2—C1—C9—C8	−0.5 (3)	C1—O1—C12—N	168.35 (14)
O1—C1—C9—C10	0.3 (3)	C1—O1—C12—C11	−12.8 (2)

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

$D-\mathrm{H}\cdots A$	$D-\mathrm{H}$	$\mathrm{H}\cdots A$	$D\cdots A$	$D-\mathrm{H}\cdots A$
N—H1*A*···O5	0.883 (9)	2.042 (16)	2.702 (2)	131 (2)
N—H1*B*···O3$^{\mathrm{i}}$	0.883 (9)	2.058 (10)	2.935 (2)	171 (2)

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

Amino atoms H1*A* and H1*B* were refined isotropically. Other H atoms were positioned geometrically and refined as riding, with C—H = 0.93–0.98 Å and $U_{\mathrm{iso}}(\mathrm{H}) = 1.2U_{\mathrm{eq}}(\mathrm{C})$. Each H atom of the *p*-tolyl methyl group is disordered over two positions of equal occupancy.

Data collection: *XSCANS* (Siemens, 1994); cell refinement: *XSCANS*; data reduction: *SHELXTL* (Bruker, 1997); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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