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3-Acetyl-7-methoxycoumarin

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Key indicators

Single-crystal X-ray study
T = 193 K
Mean σ(C–C) = 0.002 Å
R factor = 0.043
wR factor = 0.118
Data-to-parameter ratio = 12.2

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

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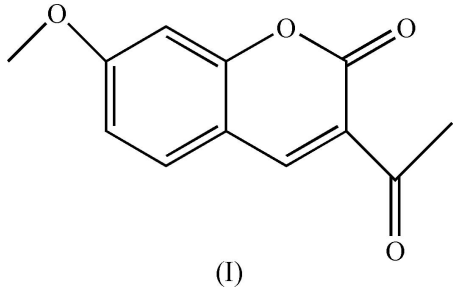
In the title molecule, $C_{12}H_{10}O_4$, the lactone and benzene rings are coplanar, while the plane of the acetyl substituent is rotated by 12.26 (9)° from the molecular plane. The molecules stack through π–π interactions along [100] and these stacks are laterally connected by C—H···O hydrogen bonds along the other two axial directions.

Comment

Coumarins are an important class of compounds because of their applications in synthetic chemistry, medicinal chemistry and photochemistry. Some coumarins are photoreactive; they are also widely used in organic solid state chemistry (Brett *et al.*, 2000; Vishnumurthy *et al.*, 2001), laser dyes (Nemkovich *et al.*, 1997; Sharma *et al.*, 2003) , biological sensors (Sardari *et al.*, 1999) and molecular switches (Maria & Wang, 2000). Coumarins exhibit antiviral (Domagala *et al.*, 1996) and antimicrobial activities (Eid *et al.*, 1994). Suitably substituted coumarins are used as nonlinear optical materials (Lindsay *et al.*, 1994). 3-Acetylcoumarin (Munshi *et al.*, 2004) displays polymorphism (Bernstein *et al.*, 1999), while many of its derivatives, such as the title compound, (I), are effective anticancer agents (Huang *et al.*, 1996) or have been proposed as sensitizers for light-sensitive materials (Donald & Samir, 1979). During our systematic search for functional organic materials, (I) was synthesized and its structure is reported here.



(I)

The title molecule (Fig. 1) is essentially planar. The lactone and benzene rings are inclined at only 0.34 (5)° to one another. The maximum deviation of the atoms in the skeleton (the lactone and benzene rings) from the molecular plane (C1–C9/O1) is only 0.0072 (11) Å. The O4/C1/O1 and C7/O3/C12 planes are inclined at 0.99 (14) and 2.95 (14)°, respectively, to the molecular plane. However, the O2/C10/C11 plane makes an angle of 12.26 (9)° with the molecular plane, and atoms O2 and C11 deviate from that plane by 0.2181 (11) and 0.2807 (11) Å. In the crystal structure, molecules stack through π–π interactions (Desiraju, 1995) (Table 3), so that

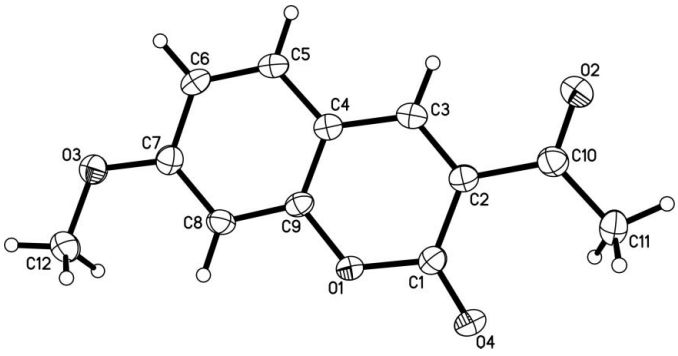


Figure 1
A view of the molecule of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 40% probability level. H atoms are represented as small spheres of arbitrary radii.

the interacting molecules are tightly and almost completely overlapped (Fig. 2). These form molecular stacks along [100], which constitute the primary stabilization of the structure. The stacks are laterally connected by relatively strong C—H···O hydrogen bonds (Desiraju, 2002) (Table 2) along [010], and the hydrogen-bonding network is further extended through other C—H···O hydrogen bonds [3.441 (2) Å] along [001], forming an ordered three-dimensional network.

Experimental

The title compound was synthesized in two steps. Firstly, 3-acetyl-7-hydoxycoumarin was prepared according to the method of Shan & Shan (1954). Next, 3-acetyl-7-hydoxycoumarin (0.01 mol), $(CH_3)_2SO_2$ (0.01 mol) and K_2CO_3 (8 g) were mixed and the mixture was refluxed in acetone (50 ml) for 3 h; the undissolved solid was filtered off and the filtrate was concentrated. The product was recrystallized three times from 95% ethanol, and light-yellow crystals of (I) were obtained from a mixture of ethanol and DMF (3:1) at room temperature over a period of two weeks (m.p. 437 K). Analysis calculated for $C_{12}H_{10}O_4$: C 66.06, H 4.59%; found: C 66.42, H 4.73%. ^{1}H NMR ($CDCl_3$, 399.97 MHz, ambient temperature): 2.17 (3H, *s*, Me), 3.92 (3H, *s*, Me), 6.84 (2H, *q*), 7.54 (1H, D), 8.51 (1H, D).

Crystal data

$C_{12}H_{10}O_4$
M_r = 218.20
Triclinic, $P\overline{1}$
a = 7.1501 (6) Å
b = 8.0640 (8) Å
c = 9.6850 (10) Å
α = 80.247 (13)°
β = 69.517 (10)°
γ = 72.896 (11)°
V = 498.60 (9) Å^3
Z = 2
D_x = 1.453 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 1600 reflections
θ = 3.1–25.3°
μ = 0.11 mm^{-1}
T = 193 (2) K
Block, light yellow
0.61 × 0.20 × 0.10 mm

Data collection

Rigaku Mercury diffractometer
ω scans
Absorption correction: multi-scan (Jacobson, 1998)
T_{min} = 0.936, T_{max} = 0.989
4889 measured reflections
1810 independent reflections
1465 reflections with $I > 2\sigma(I)$
R_{int} = 0.018
θ_{max} = 25.4°
$h = -8 \rightarrow 8$
$k = -9 \rightarrow 9$
$l = -11 \rightarrow 11$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.043
$wR(F^2)$ = 0.118
S = 1.07
1810 reflections
148 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0649P)^2 + 0.0595P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.27 e Å^{-3}
$\Delta\rho_{min}$ = −0.22 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

O1—C9	1.3729 (16)	O3—C12	1.4348 (17)
O1—C1	1.3911 (17)	O4—C1	1.2019 (17)
O2—C10	1.2176 (18)	C2—C10	1.491 (2)
O3—C7	1.3531 (17)	C10—C11	1.493 (2)
C7—O3—C12	117.84 (11)	C1—C2—C10	121.32 (12)
O4—C1—O1	115.36 (12)	O3—C7—C8	123.66 (13)
O4—C1—C2	128.03 (14)	O3—C7—C6	115.61 (12)
O1—C1—C2	116.60 (12)	C8—C7—C6	120.73 (13)
C3—C2—C1	119.70 (13)	O2—C10—C2	118.91 (13)
C3—C2—C10	118.98 (13)	O2—C10—C11	119.91 (14)
C9—O1—C1—O4	179.41 (11)	C12—O3—C7—C8	−2.4 (2)
C9—O1—C1—C2	0.32 (19)	C12—O3—C7—C6	177.23 (13)
O4—C1—C2—C3	−179.12 (14)	C3—C2—C10—O2	12.4 (2)
O1—C1—C2—C3	−0.2 (2)	C1—C2—C10—O2	−167.91 (14)
O4—C1—C2—C10	1.2 (2)	C3—C2—C10—C11	−167.29 (13)
O1—C1—C2—C10	−179.82 (11)	C1—C2—C10—C11	12.4 (2)
C10—C2—C3—C4	179.87 (11)		

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

D—H···A	D—H	H···A	D···A	D—H···A
C12—H12B···O3^{i}	0.98	2.58	3.4406 (19)	147
C3—H3···O2^{ii}	0.95	2.37	3.2726 (17)	158

Symmetry codes: (i) $-x+1, -y+3, -z+2$; (ii) $-x+2, -y+1, -z+1$.

Table 3
π–π Interactions in the title crystal (Å, °).

$d_{p\cdots p}$	$d_{c\cdots c}$	ANP	Symmetry code
3.37	3.51	16.1	$2-x, 2-y, 1-z$
3.36	4.08	34.6	$1-x, 2-y, 1-z$

Notes: $d_{p\cdots p}$: distances between the least squares molecular planes. $d_{c\cdots c}$: distances between the centroids of the ring planes. ANP: angle between the ring centroid vectors and the normal to the ring plane.

All H atoms were refined using a riding model, with C—H = 0.95 Å and U_{iso}(H) = 1.2U_{eq}(C) for aromatic and C—H = 0.98 Å and U_{iso}(H) = 1.5U_{eq}(C) for methyl H atoms.

Data collection: *CrystalClear* (Rigaku, 1999; Pflugrath, 1999); cell refinement: *CrystalClear*; data reduction: *CrystalStructure* (Rigaku/MSC, 2000); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *CrystalStructure*.

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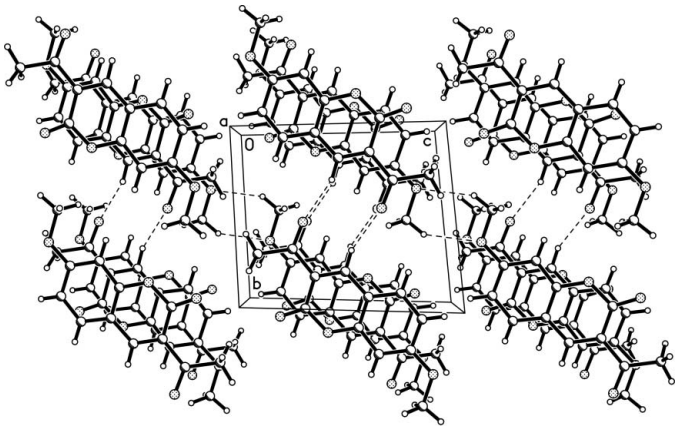

Figure 2
Packing diagram, viewed down the *a* axis. Dashed lines indicate weak C—H···O interactions.

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