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2-Oxo-2*H*-chromen-3-yl 4-*tert*-butylbenzoate

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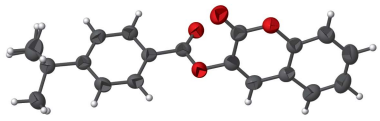
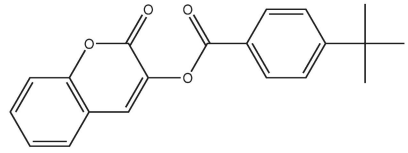
In the title coumarin derivative, $C_{20}H_{18}O_4$, the benzene ring of the benzoate group is oriented at a dihedral angle of 57.55 (9)° with respect to the planar chromene ring system [maximum deviation from plane is 0.027 (2) Å]. In the crystal, inversion-related molecules are linked into dimers *via* C—H···O hydrogen bonds, generating $R_2^2(12)$ loops. The dimers are linked by further C—H···O hydrogen bonds forming layers, parallel to the *bc* plane, which are linked *via* C—H···π interactions, forming a three-dimensional framework

3D view



Chemical scheme



Structure description

Coumarins are bioactive substances of the benzo-α-pyrone family and are of great interest due to their pharmacological properties, showing antioxidant, antiviral and anti-inflammatory effects, among others (Francisco *et al.*, 2016). In particular, the physiological, bacteriostatic and anti-tumor activities make these compounds attractive for backbone derivatization and screening as novel therapeutic agents (Jain *et al.*,2012). They possess a conjugated system with good charge-transport properties (Murray *et al.*,1982). Coumarins have a sweet odor, easily recognized by the scent of new-mown hay, and hence they have been used in perfumes since 1882. It is presumed to be produced by plants as a chemical defense to discourage predation. In another important application, coumarin dyes are extensively used as gain media in blue–green tunable organic dye lasers (Schäfer, 1990; Duarte & Hillman, 1990; Duarte, 2003). They are also used as the active medium in coherent OLED emitters (Duarte *et al.*, 2005). As part of our ongoing studies in this area, we now describe the synthesis and the crystal structure of the title coumarin derivative which has a benzoate substituent at position 3 of the coumarin ring

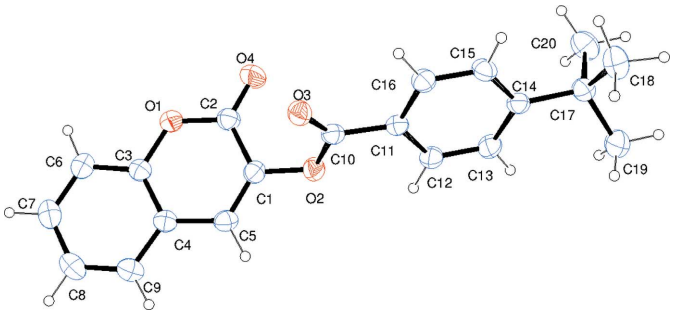


Figure 1
The molecular structure of the title compound, with atom labelling. Displacement ellipsoids are drawn at the 30% probability level.

system (Fig. 1). Our group has previously reported a number of related structures (Abou *et al.*, 2011, 2012*a*,*b*, Abou *et al.*, 2013).

In the title compound, Fig. 1, the benzene ring is inclined to the coumarin ring by 57.55 (9)°. The bond lengths and angles in the title molecule are similar to those observed for the 4-methylbenzoate analogue, 2-oxo-2*H*-chromen-3-yl 4-methylbenzoate (Matos *et al.*, 2013). There, however, the benzene ring is inclined to the coumarin ring by 79.64 (5)°.

In the crystal, molecules are linked by pairs of C6—H6···O4^{ii} hydrogen bonds, forming inversion dimers that generate $R_2^2(12)$ ring motifs (Table 1 and Fig. 2). The dimers are linked by further C—H···O hydrogen bonds, forming layers parallel to the *bc* plane (Table 1). The layers are linked *via* C—H···π interactions, forming a three-dimensional framework (Table 1).

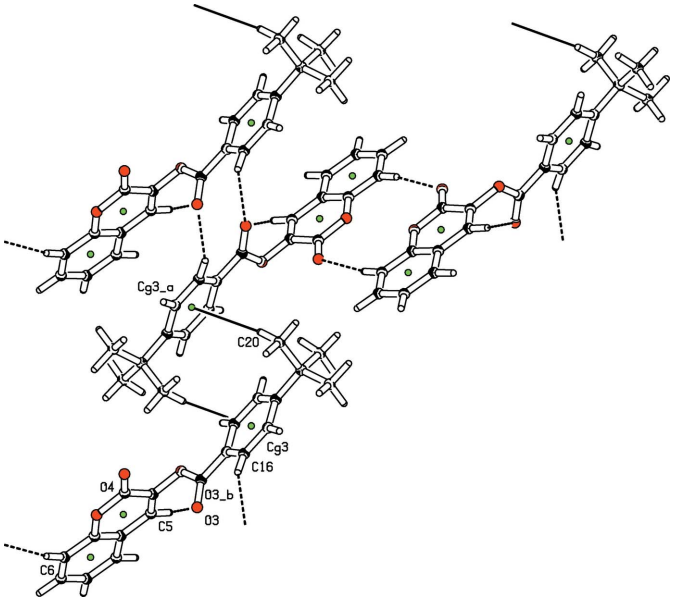


Figure 2
Part of the crystal packing of the title compound, showing the formation of $R_2^2(12)$ cyclic dimers. Dashed lines indicate hydrogen-bond contacts. H atoms not involved in hydrogen-bond interactions have been omitted for clarity. C—H···π interactions are shown as black lines. The green circles indicate ring centroids.

Table 1
Hydrogen-bond geometry (Å, °).

*Cg*3 is the centroid of the C11–C16 ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C5—H5···O3^{i}	0.96 (3)	2.52 (3)	3.433 (3)	158 (2)
C6—H6···O4^{ii}	0.97 (3)	2.40 (3)	3.360 (3)	170 (2)
C16—H16···O3^{iii}	0.98 (2)	2.57 (2)	3.495 (3)	157.1 (19)
C20—H20*C*···*Cg*3^{iv}	1.02 (4)	2.91 (4)	3.892 (4)	162 (3)

Symmetry codes: (i) $x, y-1, z$; (ii) $-x+\frac{1}{2}, -y+\frac{3}{2}, -z$; (iii) $-x+\frac{1}{2}, y+\frac{1}{2}, -z+\frac{1}{2}$; (iv) $-x+1, y, -z+\frac{1}{2}$.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{20}H_{18}O_4$
M_r	322.34
Crystal system, space group	Monoclinic, *C*2/*c*
Temperature (K)	298
a, *b*, *c* (Å)	22.8977 (5), 5.9947 (1), 24.0352 (7)
β (°)	93.297 (2)
V (Å^3)	3293.73 (13)
Z	8
Radiation type	Mo *K*α
μ (mm^{-1})	0.09
Crystal size (mm)	0.36 × 0.16 × 0.03
Data collection	
Diffractometer	Agilent SuperNova Dual diffractometer with an Atlas detector
Absorption correction	Multi-scan (*CrysAlis PRO*; Agilent, 2011)
T_{min}, T_{max}	0.668, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	19994, 3005, 2740
R_{int}	0.031
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.602
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.048, 0.127, 1.12
No. of reflections	3005
No. of parameters	290
H-atom treatment	All H-atom parameters refined
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.21, −0.19

Computer programs: *CrysAlis PRO* (Agilent, 2011), *SHELXS2013* (Sheldrick, 2008), *SHELXL2013* (Sheldrick, 2015), *ORTEP-3 for Windows* (Farrugia, 2012), *PLATON* (Spek, 2009) and *publCIF* (Westrip, 2010).

Synthesis and crystallization

Dried triethylamine (3 mol) was add to a solution of 4-*tert*-butylbenzoyl chloride (6.17 10 $^{-3}$ mol) in dried tetrahydrofuran (31 ml). While stirring vigorously, 6.17 10 $^{-3}$ mol of chroman-2,3-dione was added in small portions over 30 min. The reaction mixture was then refluxed for 4 h and poured in a separatory funnel containing 40 ml of chloroform. The solution was acidified with dilute hydrochloric acid until the pH changed to 2–3. The organic layer was extracted, washed with water until neutral, dried over $MgSO_4$ and the solvent removed *in vacuo*. The resulting precipitate (crude product) was filtered off with suction, washed with petroleum ether and dissolved in a minimum of chloroform by heating under agitation. Hexane was added to this hot mixture until the formation of a new precipitate started, which dissolved in the resulting mixture upon heating. While cooling, colourless

crystals of the title compound suitable for X-ray diffraction analysis were formed (yield of 84%, m.p. 413-410 K).

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

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full crystallographic data

IUCrData (2016). **1**, x161633 [https://doi.org/10.1107/S2414314616016333]

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2-Oxo-2*H*-chromen-3-yl 4-*tert*-butylbenzoate

Crystal data

$C_{20}H_{18}O_4$
M_r = 322.34
Monoclinic, $C2/c$
a = 22.8977 (5) Å
b = 5.9947 (1) Å
c = 24.0352 (7) Å
β = 93.297 (2)°
V = 3293.73 (13) Å^3
Z = 8
$F(000)$ = 1360
D_x = 1.300 Mg m^{-3}
Melting point: 413 K
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 11432 reflections
θ = 5.2–68.2°
μ = 0.09 mm^{-1}
T = 298 K
Prism, colorless
0.36 × 0.16 × 0.03 mm

Data collection

Agilent SuperNova Dual diffractometer with an Atlas detector
Radiation source: sealed X-ray tube
Detector resolution: 5.3048 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (CrysAlis PRO; Agilent, 2011)
T_{min} = 0.668, T_{max} = 1.000
19994 measured reflections
3005 independent reflections
2740 reflections with $I > 2\sigma(I)$
R_{int} = 0.031
θ_{max} = 25.4°, θ_{min} = 1.7°
h = −27→27
k = −7→7
l = −28→28

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.048
$wR(F^2)$ = 0.127
S = 1.12
3005 reflections
290 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: difference Fourier map
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0332P)^2 + 4.6284P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.008
$\Delta\rho_{max}$ = 0.21 e Å^{-3}
$\Delta\rho_{min}$ = −0.19 e Å^{-3}
Extinction correction: SHELXL, $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.0015 (2)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
H16	0.3272 (10)	1.023 (4)	0.2757 (10)	0.062 (7)*
H5	0.2542 (10)	0.138 (4)	0.1680 (10)	0.065 (7)*
H9	0.1764 (11)	−0.075 (5)	0.1146 (11)	0.070 (8)*
H13	0.4819 (12)	0.528 (5)	0.3157 (11)	0.075 (8)*
H12	0.4071 (11)	0.422 (5)	0.2516 (10)	0.070 (8)*
H15	0.3990 (11)	1.118 (5)	0.3411 (11)	0.073 (8)*
H7	0.1090 (12)	0.155 (5)	−0.0363 (12)	0.084 (9)*
H6	0.1705 (12)	0.474 (5)	−0.0253 (12)	0.079 (9)*
H18B	0.5169 (14)	1.105 (5)	0.4499 (13)	0.098 (10)*
H18C	0.4654 (15)	1.217 (6)	0.4040 (15)	0.114 (12)*
H18A	0.4507 (14)	0.979 (6)	0.4427 (13)	0.098 (10)*
H19C	0.5502 (14)	0.619 (6)	0.3749 (13)	0.091 (11)*
H19B	0.5623 (15)	0.762 (5)	0.4318 (13)	0.100 (10)*
H20A	0.5254 (15)	1.161 (6)	0.3205 (14)	0.107 (12)*
H8	0.1130 (12)	−0.124 (5)	0.0327 (11)	0.084 (9)*
H20B	0.5787 (14)	1.082 (6)	0.3666 (13)	0.098 (10)*
H20C	0.5607 (15)	0.933 (6)	0.3108 (15)	0.115 (12)*
H19A	0.5026 (19)	0.623 (7)	0.4250 (17)	0.137 (16)*
O1	0.24340 (7)	0.5617 (3)	0.05360 (6)	0.0546 (4)
O2	0.32331 (7)	0.4732 (3)	0.18668 (6)	0.0531 (4)
O3	0.26552 (6)	0.7562 (3)	0.21178 (6)	0.0538 (4)
C1	0.28335 (9)	0.4315 (4)	0.14183 (9)	0.0478 (5)
C12	0.40656 (10)	0.5701 (4)	0.27018 (10)	0.0533 (6)
C10	0.31100 (9)	0.6565 (4)	0.21793 (9)	0.0459 (5)
O4	0.31340 (8)	0.7596 (3)	0.09731 (7)	0.0700 (5)
C5	0.25118 (10)	0.2475 (4)	0.13885 (9)	0.0489 (5)
C2	0.28268 (10)	0.5978 (4)	0.09770 (9)	0.0515 (5)
C11	0.35955 (9)	0.7120 (3)	0.25861 (8)	0.0434 (5)
C3	0.20823 (9)	0.3749 (4)	0.05008 (9)	0.0469 (5)
C17	0.50185 (10)	0.9101 (4)	0.37556 (10)	0.0537 (6)
C14	0.45086 (9)	0.8370 (4)	0.33559 (9)	0.0459 (5)
C4	0.21134 (9)	0.2126 (4)	0.09126 (9)	0.0471 (5)
C15	0.40346 (10)	0.9760 (4)	0.32324 (10)	0.0528 (6)
C16	0.35827 (10)	0.9159 (4)	0.28567 (10)	0.0503 (5)
C9	0.17480 (11)	0.0272 (4)	0.08422 (11)	0.0591 (6)
C13	0.45114 (10)	0.6337 (4)	0.30808 (10)	0.0555 (6)
C6	0.17062 (11)	0.3582 (5)	0.00291 (10)	0.0571 (6)
C8	0.13727 (12)	0.0079 (5)	0.03776 (12)	0.0682 (7)
C7	0.13535 (11)	0.1724 (5)	−0.00266 (12)	0.0652 (7)

C18	0.48124 (14)	1.0693 (6)	0.42020 (13)	0.0742 (8)
C19	0.53159 (19)	0.7113 (6)	0.4051 (2)	0.0958 (13)
C20	0.54615 (13)	1.0336 (6)	0.34139 (15)	0.0732 (8)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0616 (9)	0.0500 (9)	0.0516 (9)	−0.0052 (7)	−0.0018 (7)	0.0076 (7)
O2	0.0572 (9)	0.0480 (9)	0.0528 (9)	0.0049 (7)	−0.0071 (7)	−0.0049 (7)
O3	0.0465 (8)	0.0524 (9)	0.0619 (10)	0.0016 (7)	−0.0013 (7)	−0.0021 (7)
C1	0.0519 (12)	0.0466 (12)	0.0446 (11)	0.0039 (10)	0.0007 (9)	−0.0020 (9)
C12	0.0625 (14)	0.0410 (12)	0.0557 (13)	0.0067 (10)	−0.0031 (11)	−0.0024 (10)
C10	0.0505 (12)	0.0408 (11)	0.0466 (12)	−0.0021 (10)	0.0045 (9)	0.0047 (9)
O4	0.0749 (11)	0.0620 (11)	0.0725 (12)	−0.0237 (9)	−0.0005 (9)	0.0102 (9)
C5	0.0602 (13)	0.0407 (11)	0.0462 (12)	0.0026 (10)	0.0064 (10)	0.0009 (10)
C2	0.0534 (12)	0.0484 (13)	0.0529 (13)	−0.0040 (10)	0.0044 (10)	0.0019 (10)
C11	0.0452 (11)	0.0396 (11)	0.0457 (11)	−0.0010 (9)	0.0047 (8)	0.0044 (9)
C3	0.0464 (11)	0.0445 (11)	0.0501 (12)	0.0021 (9)	0.0060 (9)	−0.0032 (9)
C17	0.0504 (12)	0.0490 (13)	0.0610 (14)	−0.0030 (10)	−0.0041 (10)	0.0006 (11)
C14	0.0457 (11)	0.0420 (11)	0.0501 (12)	−0.0020 (9)	0.0033 (9)	0.0045 (9)
C4	0.0499 (11)	0.0430 (11)	0.0490 (12)	0.0024 (9)	0.0087 (9)	−0.0037 (9)
C15	0.0519 (12)	0.0396 (12)	0.0664 (15)	0.0014 (10)	−0.0011 (10)	−0.0061 (11)
C16	0.0453 (11)	0.0447 (12)	0.0605 (14)	0.0063 (10)	0.0010 (10)	−0.0017 (10)
C9	0.0669 (15)	0.0502 (14)	0.0609 (15)	−0.0073 (12)	0.0108 (12)	−0.0036 (12)
C13	0.0538 (13)	0.0480 (13)	0.0637 (14)	0.0134 (11)	−0.0056 (11)	−0.0006 (11)
C6	0.0578 (13)	0.0611 (15)	0.0522 (13)	0.0074 (12)	0.0001 (11)	−0.0006 (12)
C8	0.0622 (15)	0.0628 (16)	0.0797 (18)	−0.0136 (13)	0.0050 (13)	−0.0163 (14)
C7	0.0539 (14)	0.0739 (18)	0.0670 (16)	0.0014 (13)	−0.0040 (12)	−0.0140 (14)
C18	0.0690 (17)	0.092 (2)	0.0607 (17)	−0.0081 (17)	0.0006 (14)	−0.0159 (16)
C19	0.095 (3)	0.069 (2)	0.116 (3)	−0.0023 (19)	−0.054 (2)	0.009 (2)
C20	0.0577 (16)	0.079 (2)	0.084 (2)	−0.0149 (15)	0.0134 (15)	−0.0106 (17)

Geometric parameters (Å, º)

O1—C2	1.367 (3)	C3—C4	1.387 (3)
O1—C3	1.379 (3)	C3—C6	1.387 (3)
O2—C10	1.369 (3)	C17—C19	1.527 (4)
O2—C1	1.396 (2)	C17—C18	1.531 (4)
O3—C10	1.203 (2)	C17—C20	1.532 (4)
C1—C5	1.326 (3)	C17—C14	1.532 (3)
C1—C2	1.455 (3)	C14—C15	1.387 (3)
C12—C13	1.382 (3)	C14—C13	1.387 (3)
C12—C11	1.387 (3)	C4—C9	1.396 (3)
C10—C11	1.476 (3)	C15—C16	1.381 (3)
O4—C2	1.198 (3)	C9—C8	1.374 (4)
C5—C4	1.437 (3)	C6—C7	1.378 (4)
C11—C16	1.386 (3)	C8—C7	1.383 (4)

C2—O1—C3	122.13 (17)	C19—C17—C18	108.0 (3)
C10—O2—C1	114.90 (16)	C19—C17—C20	109.6 (3)
C5—C1—O2	121.9 (2)	C18—C17—C20	108.3 (2)
C5—C1—C2	123.2 (2)	C19—C17—C14	111.8 (2)
O2—C1—C2	114.77 (19)	C18—C17—C14	111.3 (2)
C13—C12—C11	119.9 (2)	C20—C17—C14	107.8 (2)
O3—C10—O2	122.38 (19)	C15—C14—C13	116.8 (2)
O3—C10—C11	125.7 (2)	C15—C14—C17	121.4 (2)
O2—C10—C11	111.92 (18)	C13—C14—C17	121.73 (19)
C1—C5—C4	119.3 (2)	C3—C4—C9	117.8 (2)
O4—C2—O1	118.8 (2)	C3—C4—C5	118.1 (2)
O4—C2—C1	125.4 (2)	C9—C4—C5	124.1 (2)
O1—C2—C1	115.80 (19)	C16—C15—C14	122.1 (2)
C16—C11—C12	118.9 (2)	C15—C16—C11	120.1 (2)
C16—C11—C10	118.31 (19)	C8—C9—C4	120.5 (3)
C12—C11—C10	122.8 (2)	C12—C13—C14	122.2 (2)
O1—C3—C4	121.33 (19)	C7—C6—C3	118.1 (2)
O1—C3—C6	116.2 (2)	C9—C8—C7	120.3 (3)
C4—C3—C6	122.5 (2)	C6—C7—C8	120.9 (2)

Hydrogen-bond geometry (Å, º)

Cg3 is the centroid of the C11–C16 ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C5—H5···O3^{i}	0.96 (3)	2.52 (3)	3.433 (3)	158 (2)
C6—H6···O4^{ii}	0.97 (3)	2.40 (3)	3.360 (3)	170 (2)
C16—H16···O3^{iii}	0.98 (2)	2.57 (2)	3.495 (3)	157.1 (19)
C20—H20*C*···*Cg*3^{iv}	1.02 (4)	2.91 (4)	3.892 (4)	162 (3)

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