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2-Oxo-2*H*-chromen-4-yl 3,3-dimethylbutanoate

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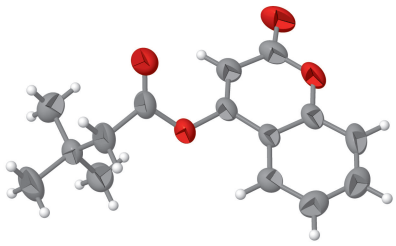
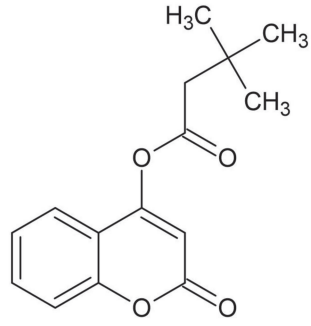
Structural data: full structural data are available from iucrdata.iucr.org

In the crystal of the title compound, $C_{15}H_{16}O_4$, the molecules are connected through C—H···O hydrogen bonds, generating [100] chains, which are cross-linked by weak π–π stacking interactions.

3D view



Chemical scheme



Structure description

Coumarin derivatives show various biological activities such as anticancer (Lacy & O'Kennedy, 2004; Kostova, 2005), anti-inflammatory (Todeschini *et al.*, 1998) and anti-viral (Borges *et al.*, 2005) properties. As part of our ongoing studies in this area (Ziki *et al.*, 2017), we now describe the synthesis and structure of the title compound, $C_{15}H_{16}O_4$.

As expected, the coumarin ring system is almost planar (r.m.s deviation = 0.025 Å) and oriented at an angle of 56.24 (18)° with the C10/C11/O3/O4 butanoate moiety (Fig. 1). The C1—C2 [1.332 (2) Å] and C2—C3 [1.446 (3) Å] bond lengths are shorter and longer, respectively, than those excepted for an aromatic C—C bond (1.38 Å). This suggests that the C1—C2 bond has significant double-bond character, as seen in other coumarin derivatives (*e.g.*, Gomes *et al.*, 2016). A short intramolecular C2—H2···O4 contact occurs (Table 1). If this is regarded as a directional bond, an *S*(6) ring is generated. In the extended structure, the molecules are linked by weak C5—H1···O1 hydrogen bonds, generating [100] *C*(6) chains (Fig. 2). Weak aromatic π–π stacking between the C4–C9 rings [centroid–centroid separation = 3.8987 (12) Å, tilt angle = 10.08 (10)°] crosslink the chains in the [001] direction.

The only red spots (close contacts) on the Hirshfeld surface of the title compound generated by *CrystalExplorer17* (Spackman *et al.*, 2021) are associated with the hydrogen-bond donor H5 and acceptor O1 atoms noted above (Fig. 3). The two-dimensional fingerprint plots (Fig. 4*a*–*e*) show that the main contributions to the

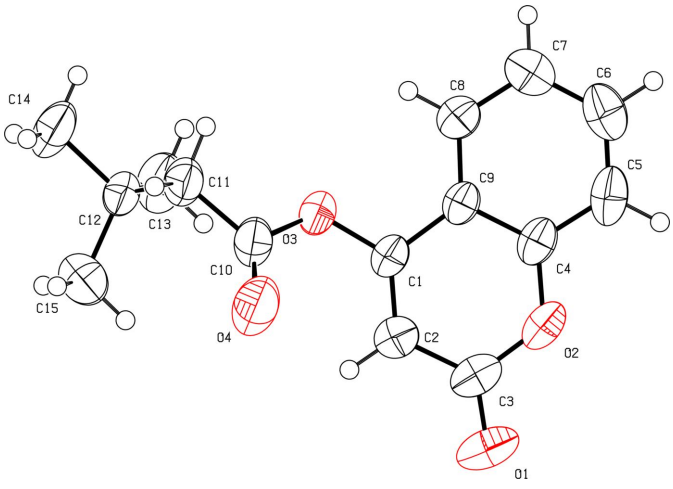


Figure 1
The molecular structure of the title compound with displacement ellipsoids drawn at the 50% probability level.

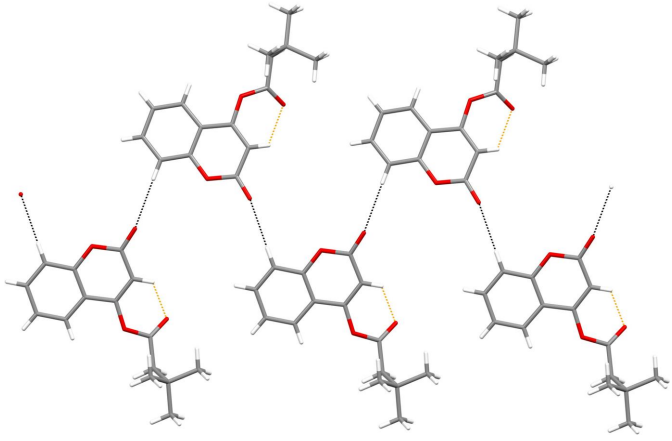


Figure 2
Part of a [100] hydrogen-bonded chain in the extended structure of the title compound. The intermolecular hydrogen bonds are shown as black dashed lines and the short intramolecular contacts as orange dashed lines.

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

D—H···A	D—H	H···A	D···A	D—H···A
C2—H2···O4	0.93	2.44	2.847 (3)	107
C5—H5···O1^{i}	0.93	2.48	3.405 (2)	176

Symmetry code: (i) $x-\frac{1}{2}, -y+\frac{1}{2}, z$.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{15}H_{16}O_4$
M_r	260.28
Crystal system, space group	Orthorhombic, $Pna2_1$
Temperature (K)	295
a, b, c (Å)	10.6769 (3), 17.9611 (5), 7.0266 (2)
V (Å^3)	1347.48 (7)
Z	4
Radiation type	Cu $K\alpha$
μ (mm^{-1})	0.76
Crystal size (mm)	0.32 × 0.18 × 0.16
Data collection	
Diffractometer	SuperNova, Dual, Cu at home/near, AtlasS2
Absorption correction	Multi-scan (*CrysAlis PRO*; Rigaku OD, 2023)
T_{min}, T_{max}	0.829, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	9694, 2249, 2133
R_{int}	0.020
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.618
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.031, 0.084, 1.05
No. of reflections	2249
No. of parameters	176
No. of restraints	1
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.11, −0.13
Absolute structure	Refined as an inversion twin.
Absolute structure parameter	0.5 (3)

Computer programs: *CrysAlis PRO* (Rigaku OD, 2023), *SHELXT2015* (Sheldrick, 2015*a*), *SHELXL2013* (Sheldrick, 2015*b*), *ORTEP-3* fro Windows (Farrugia, 2012) and *publCIF* (Westrip, 2010).

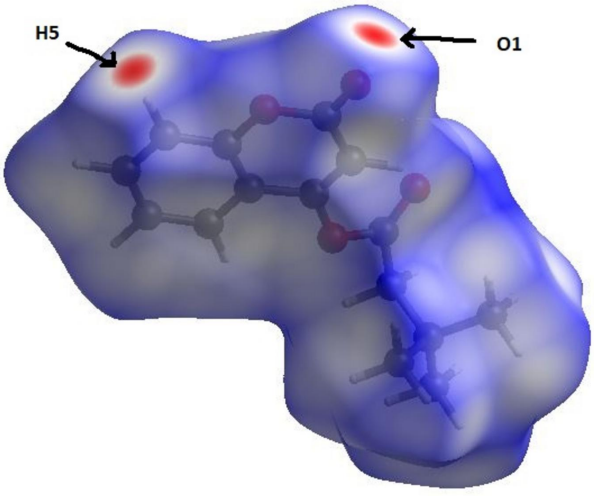


Figure 3
A view of the Hirshfeld surface mapped over d_{norm}. The short contact points (red) are labelled to indicate the atoms participating in the intermolecular interactions.

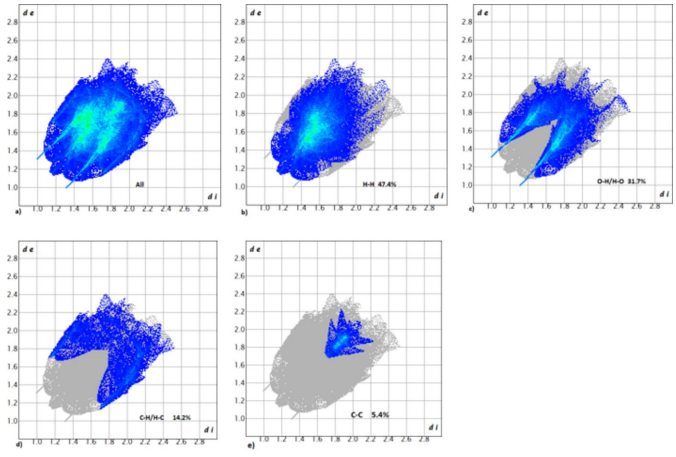


Figure 4
Two-dimensional fingerprint plots: (*a*) overall, and delineated into contributions from different contacts: (*b*) H···H, (*c*) H···O/O···H, (*d*) H···C/C···H and (*e*) C···C.

Hirshfeld surface are H···H, H···O/O···H, H···C/C···H and C···C contacts, which contribute 47.4, 31.7, 14.2 and 5.4%, respectively.

Synthesis and crystallization

In a 100 ml round-necked flask topped with a water condenser were introduced successively: dried diethyl ether (16 ml), *tert*-butylacetyl chloride (0.90 ml, 6.2 mmol) and dried pyridine (2.31 ml, 4.7 molar equivalents). With vigorous stirring, 4-hydroxycoumarin (1.00 g; 6.17 mmol) was added in small portions over 30 min. The reaction mixture was left stirring at room temperature for 3 h. The mixture was then poured in a separating funnel containing 40 ml of chloroform and washed with diluted hydrochloric acid solution until the pH was 2–3. The organic phase was extracted, washed with water to neutrality, dried over $MgSO_4$ and the solvent removed. The resulting precipitate was filtered off with suction, washed with *n*-pentane and recrystallized from acetone solution to obtain colourless prisms of the title compound: yield 63%; m.p. 430–431 K

Refinement

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

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full crystallographic data

IUCrData (2024). **9**, x240494 [https://doi.org/10.1107/S2414314624004942]

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Crystal data

$C_{15}H_{16}O_4$
M_r = 260.28
Orthorhombic, $Pna2_1$
a = 10.6769 (3) Å
b = 17.9611 (5) Å
c = 7.0266 (2) Å
V = 1347.48 (7) Å^3
Z = 4
$F(000)$ = 552
D_x = 1.283 Mg m^{-3}
Melting point: 430 K
Cu $K\alpha$ radiation, λ = 1.54184 Å
Cell parameters from 6044 reflections
θ = 4.8–72.4°
μ = 0.76 mm^{-1}
T = 295 K
Prism, colourless
0.32 × 0.18 × 0.16 mm

Data collection

SuperNova, Dual, Cu at home/near, AtlasS2 diffractometer
Radiation source: micro-focus sealed X-ray tube; SuperNova (Cu) X-ray Source
Mirror monochromator
ω scan
Absorption correction: multi-scan (CrysAlis PRO; Rigaku OD, 2023)
T_{min} = 0.829, T_{max} = 1.000
9694 measured reflections
2249 independent reflections
2133 reflections with $I > 2\sigma(I)$
R_{int} = 0.020
θ_{max} = 72.4°, θ_{min} = 4.8°
h = −12→13
k = −22→21
l = −8→7
2249 standard reflections every 25 min

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.031
$wR(F^2)$ = 0.084
S = 1.05
2249 reflections
176 parameters
1 restraint
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.049P)^2 + 0.0768P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.11 e Å^{-3}
$\Delta\rho_{min}$ = −0.13 e Å^{-3}
Absolute structure: Refined as an inversion twin.
Absolute structure parameter: 0.5 (3)

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.

Refinement. Refined as a 2-component inversion twin.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.81314 (18)	0.29193 (8)	0.4568 (3)	0.0877 (6)
O2	0.62460 (14)	0.33944 (6)	0.4897 (2)	0.0631 (4)
O3	0.76506 (11)	0.55295 (6)	0.5416 (2)	0.0578 (4)
O4	0.93542 (18)	0.52915 (9)	0.7209 (4)	0.0924 (7)
C1	0.72707 (16)	0.47995 (8)	0.5255 (3)	0.0468 (4)
C2	0.80284 (18)	0.42179 (10)	0.5013 (4)	0.0569 (4)
H2	0.8891	0.4290	0.4974	0.068*
C3	0.7522 (2)	0.34755 (10)	0.4809 (3)	0.0615 (5)
C4	0.54603 (17)	0.39958 (9)	0.5092 (3)	0.0504 (4)
C5	0.4183 (2)	0.38581 (12)	0.5105 (3)	0.0650 (5)
H5	0.3882	0.3373	0.5014	0.078*
C6	0.33703 (19)	0.44444 (14)	0.5253 (3)	0.0673 (6)
H6	0.2512	0.4356	0.5262	0.081*
C7	0.38128 (18)	0.51700 (12)	0.5390 (3)	0.0623 (5)
H7	0.3252	0.5565	0.5470	0.075*
C8	0.50808 (17)	0.53037 (10)	0.5406 (3)	0.0515 (4)
H8	0.5375	0.5789	0.5509	0.062*
C9	0.59267 (16)	0.47158 (8)	0.5268 (3)	0.0435 (4)
C10	0.87001 (19)	0.57316 (12)	0.6437 (4)	0.0583 (5)
C11	0.8867 (2)	0.65593 (11)	0.6425 (4)	0.0604 (5)
H11A	0.9275	0.6707	0.7599	0.072*
H11B	0.8046	0.6792	0.6401	0.072*
C12	0.96367 (16)	0.68573 (9)	0.4739 (3)	0.0516 (4)
C13	0.9024 (3)	0.66854 (15)	0.2840 (4)	0.0798 (7)
H13A	0.8958	0.6156	0.2684	0.120*
H13B	0.9523	0.6889	0.1830	0.120*
H13C	0.8203	0.6903	0.2806	0.120*
C14	0.9745 (3)	0.77005 (12)	0.5023 (6)	0.0868 (8)
H14A	0.8922	0.7915	0.5070	0.130*
H14B	1.0204	0.7914	0.3983	0.130*
H14C	1.0175	0.7801	0.6195	0.130*
C15	1.0947 (2)	0.65202 (14)	0.4765 (5)	0.0739 (6)
H15A	1.1348	0.6636	0.5952	0.111*
H15B	1.1430	0.6722	0.3735	0.111*
H15C	1.0889	0.5990	0.4626	0.111*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.1116 (13)	0.0485 (8)	0.1030 (14)	0.0254 (8)	−0.0004 (12)	−0.0058 (9)
O2	0.0819 (9)	0.0344 (6)	0.0732 (10)	−0.0071 (5)	−0.0018 (9)	0.0023 (7)
O3	0.0523 (6)	0.0387 (6)	0.0824 (10)	−0.0079 (5)	−0.0064 (7)	0.0043 (6)
O4	0.0924 (12)	0.0634 (9)	0.1214 (18)	−0.0185 (9)	−0.0473 (12)	0.0232 (10)
C1	0.0538 (9)	0.0364 (8)	0.0503 (10)	−0.0053 (6)	0.0001 (9)	0.0039 (8)
C2	0.0570 (9)	0.0482 (9)	0.0654 (12)	0.0032 (7)	0.0014 (10)	0.0019 (10)
C3	0.0812 (13)	0.0434 (9)	0.0598 (13)	0.0092 (9)	−0.0012 (12)	0.0017 (9)
C4	0.0656 (10)	0.0421 (8)	0.0436 (9)	−0.0100 (7)	−0.0008 (9)	0.0045 (8)
C5	0.0738 (12)	0.0637 (11)	0.0574 (12)	−0.0302 (10)	−0.0038 (11)	0.0092 (11)
C6	0.0533 (10)	0.0923 (15)	0.0563 (12)	−0.0153 (10)	0.0005 (11)	0.0094 (13)
C7	0.0545 (10)	0.0762 (13)	0.0562 (11)	0.0065 (9)	0.0010 (10)	0.0033 (11)
C8	0.0579 (9)	0.0468 (9)	0.0498 (10)	0.0003 (7)	−0.0009 (9)	0.0014 (8)
C9	0.0527 (8)	0.0381 (7)	0.0397 (8)	−0.0065 (6)	0.0001 (8)	0.0039 (7)
C10	0.0575 (10)	0.0514 (10)	0.0660 (12)	−0.0137 (9)	−0.0017 (10)	0.0029 (10)
C11	0.0597 (11)	0.0497 (10)	0.0716 (13)	−0.0117 (8)	0.0073 (10)	−0.0099 (10)
C12	0.0525 (9)	0.0398 (8)	0.0626 (12)	−0.0086 (7)	−0.0034 (9)	−0.0019 (8)
C13	0.0913 (17)	0.0747 (16)	0.0733 (16)	−0.0182 (13)	−0.0236 (13)	0.0109 (13)
C14	0.1012 (16)	0.0441 (10)	0.115 (2)	−0.0192 (10)	0.0060 (19)	−0.0045 (14)
C15	0.0576 (11)	0.0847 (14)	0.0793 (16)	−0.0015 (10)	0.0018 (12)	−0.0032 (13)

Geometric parameters (Å, º)

O1—C3	1.204 (2)	C8—C9	1.393 (2)
O2—C3	1.371 (3)	C8—H8	0.9300
O2—C4	1.374 (2)	C10—C11	1.497 (3)
O3—C1	1.3771 (19)	C11—C12	1.538 (3)
O3—C10	1.379 (2)	C11—H11A	0.9700
O4—C10	1.186 (3)	C11—H11B	0.9700
C1—C2	1.332 (2)	C12—C13	1.518 (3)
C1—C9	1.443 (2)	C12—C15	1.525 (3)
C2—C3	1.446 (3)	C12—C14	1.532 (3)
C2—H2	0.9300	C13—H13A	0.9600
C4—C5	1.386 (3)	C13—H13B	0.9600
C4—C9	1.391 (2)	C13—H13C	0.9600
C5—C6	1.368 (3)	C14—H14A	0.9600
C5—H5	0.9300	C14—H14B	0.9600
C6—C7	1.390 (3)	C14—H14C	0.9600
C6—H6	0.9300	C15—H15A	0.9600
C7—C8	1.375 (3)	C15—H15B	0.9600
C7—H7	0.9300	C15—H15C	0.9600
C3—O2—C4	121.82 (13)	O3—C10—C11	110.79 (18)
C1—O3—C10	122.19 (15)	C10—C11—C12	114.42 (18)
C2—C1—O3	125.33 (16)	C10—C11—H11A	108.7
C2—C1—C9	121.53 (15)	C12—C11—H11A	108.7

O3—C1—C9	113.06 (14)	C10—C11—H11B	108.7
C1—C2—C3	120.57 (18)	C12—C11—H11B	108.7
C1—C2—H2	119.7	H11A—C11—H11B	107.6
C3—C2—H2	119.7	C13—C12—C15	109.0 (2)
O1—C3—O2	117.08 (19)	C13—C12—C14	110.4 (2)
O1—C3—C2	125.2 (2)	C15—C12—C14	108.79 (17)
O2—C3—C2	117.71 (16)	C13—C12—C11	112.06 (17)
O2—C4—C5	117.45 (16)	C15—C12—C11	110.08 (19)
O2—C4—C9	121.39 (16)	C14—C12—C11	106.50 (19)
C5—C4—C9	121.16 (18)	C12—C13—H13A	109.5
C6—C5—C4	119.15 (18)	C12—C13—H13B	109.5
C6—C5—H5	120.4	H13A—C13—H13B	109.5
C4—C5—H5	120.4	C12—C13—H13C	109.5
C5—C6—C7	120.76 (18)	H13A—C13—H13C	109.5
C5—C6—H6	119.6	H13B—C13—H13C	109.5
C7—C6—H6	119.6	C12—C14—H14A	109.5
C8—C7—C6	119.95 (19)	C12—C14—H14B	109.5
C8—C7—H7	120.0	H14A—C14—H14B	109.5
C6—C7—H7	120.0	C12—C14—H14C	109.5
C7—C8—C9	120.36 (17)	H14A—C14—H14C	109.5
C7—C8—H8	119.8	H14B—C14—H14C	109.5
C9—C8—H8	119.8	C12—C15—H15A	109.5
C4—C9—C8	118.61 (16)	C12—C15—H15B	109.5
C4—C9—C1	116.89 (15)	H15A—C15—H15B	109.5
C8—C9—C1	124.49 (15)	C12—C15—H15C	109.5
O4—C10—O3	122.75 (19)	H15A—C15—H15C	109.5
O4—C10—C11	126.5 (2)	H15B—C15—H15C	109.5

C10—O3—C1—C2	−40.0 (3)	C5—C4—C9—C8	−1.7 (3)
C10—O3—C1—C9	143.23 (18)	O2—C4—C9—C1	−0.6 (3)
O3—C1—C2—C3	−178.33 (19)	C5—C4—C9—C1	179.5 (2)
C9—C1—C2—C3	−1.8 (3)	C7—C8—C9—C4	0.7 (3)
C4—O2—C3—O1	−177.4 (2)	C7—C8—C9—C1	179.4 (2)
C4—O2—C3—C2	2.6 (3)	C2—C1—C9—C4	2.5 (3)
C1—C2—C3—O1	179.2 (2)	O3—C1—C9—C4	179.41 (17)
C1—C2—C3—O2	−0.7 (3)	C2—C1—C9—C8	−176.2 (2)
C3—O2—C4—C5	178.0 (2)	O3—C1—C9—C8	0.7 (3)
C3—O2—C4—C9	−1.9 (3)	C1—O3—C10—O4	1.4 (4)
O2—C4—C5—C6	−178.5 (2)	C1—O3—C10—C11	−178.15 (18)
C9—C4—C5—C6	1.4 (3)	O4—C10—C11—C12	91.9 (3)
C4—C5—C6—C7	0.0 (4)	O3—C10—C11—C12	−88.6 (2)
C5—C6—C7—C8	−1.0 (4)	C10—C11—C12—C13	61.4 (2)
C6—C7—C8—C9	0.6 (3)	C10—C11—C12—C15	−60.0 (2)
O2—C4—C9—C8	178.16 (18)	C10—C11—C12—C14	−177.8 (2)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C2—H2···O4	0.93	2.44	2.847 (3)	107
C5—H5···O1^{i}	0.93	2.48	3.405 (2)	176

Symmetry code: (i) $x-1/2, -y+1/2, z$.