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2-(4-Chlorophenyl)-3-hydroxy-4*H*-chromen-4-one

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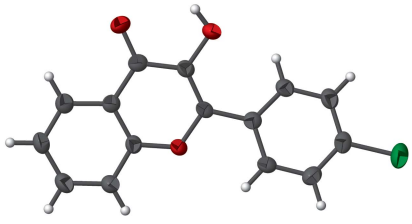
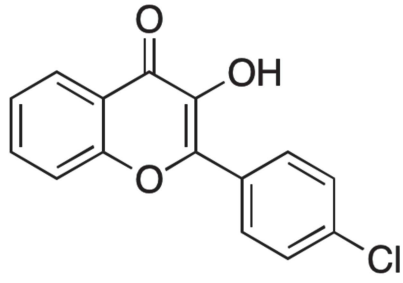
Structural data: full structural data are available from iucrdata.iucr.org

Flavones are a subclass of flavonoids, secondary metabolites of plants which contain the 2-phenylbenzopyran pharmacophore. They are of interest as they display a wide variety of biological activities, such as anticancer and antioxidant. Recently, there has been an interest in coordinating flavones to various transition metals for anticancer activity. Our work in this area led to the synthesis and crystallization of flavones as intermediates. Herein, we report the first crystal structure of 2-(4-chlorophenyl)-3-hydroxy-4*H*-chromen-4-one, $C_{15}H_9ClO_3$, a well studied compound.

3D view



Chemical scheme



Structure description

In the crystal structure of the title compound (Fig. 1), the molecules form hydrogen-bonded dimers (Table 1) between the molecule and an inversion-related adjacent molecule. The hydrogen-bonding occurs between oxygen atoms on the benzopyranone ring, with a classical R_2^2 (10) synthon. The O1^{i} $\cdots$O3 hydrogen-bond distance is 2.698 (3) Å [symmetry code: (i) $-x$, $-y+2$, $-z+1$]. The molecule is nearly planar with the phenyl ring tilted 15.92 (8)° with respect to the benzopyranone ring. The overall structure forms a herringbone pattern (Fig. 2) with each block consisting of molecular dimers, the layers are held together with π–π interactions and π–Br interactions. The layers have a parallel displacement that results in a Br1$\cdots$*Cg*1^{ii} π–Br interaction with a distance of 3.623 (3) Å [symmetry code: (ii) x, $y-1$, z; *Cg*1 is the centroid of the chlorophenyl ring] and a *Cg*2$\cdots$*Cg*1^{ii} π–π interaction with a distance of 3.688 (2) Å. (*Cg*2 is the centroid of the pyranone ring).

Synthesis and crystallization

The title compound was synthesized from the aldol condensation of 2-hydroxyacetophenone and 4-chlorobenzaldehyde to yield the chalcone (*E*)-3-(4-chlorophenyl)-1-(2-

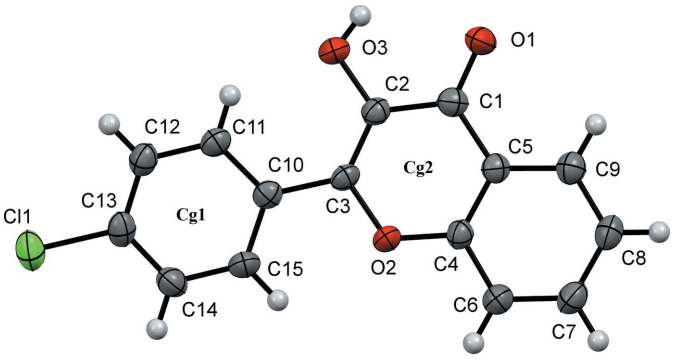


Figure 1
A view of the molecular structure of the title compound, showing the atom labeling. Displacement ellipsoids are drawn at the 50% probability level.

hydroxyphenyl)prop-2-en-1-one followed by its oxidative cyclization to the flavone, as reported in the literature (Kurzwernhart *et al.*, 2012), see Fig. 3. 2-Hydroxyacetophenone (136 mg, 1 mmol) and 4-chlorobenzaldehyde (141 mg, 1 mmol) were dissolved in ethanol (5 ml). An NaOH solution (5 *M*, 1 ml) was added and the reaction was stirred until a precipitate formed. The reaction mixture was cooled in an ice bath for 20 min. The solids were filtered and taken directly to the next step. (*E*)-3-(4-Chlorophenyl)-1-(2-hydroxyphenyl)prop-2-en-1-one was then suspended in EtOH (5 ml) and cooled in an ice–water bath. An NaOH solution (5 *M*, 1 ml) and H_2O_2 (30%, 2.2 equiv, 0.25 ml) were added and the reaction stirred overnight, warming to room temperature. The reaction mixture was acidified to pH 1 with HCl (6 *M*) and poured into cold water. The yellow solid was collected by filtration and slow evaporation of a solution of the title compound in MeOH gave yellow crystals (64 mg, 24% yield over two steps). The structure was confirmed to match the literature (Kurzwernhart *et al.*, 2012) NMR: ^{1}H NMR [300 MHz, $(CD_3)_2SO$)] δ = 8.24 (*bs*, 1H), 8.22 (*d*, *J* = 8.7 Hz, 2H), 8.07 (*d*, *J* = 7.5 Hz, 1H), 7.81–7.71 (*m*, 2H), 7.60 (*d*, *J* = 8.4 Hz, 2H), 7.44 (*t*, *J* = 7.2 Hz, 1H) p.p.m..

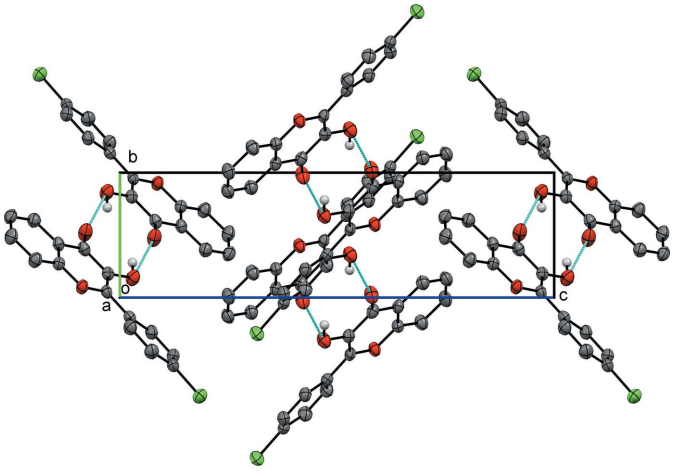


Figure 2
Crystal packing diagram of the title compound viewed along the *a* axis, H atoms have been omitted for clarity.

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H3···O1^{i}	0.84 (5)	1.95 (5)	2.698 (3)	149 (4)

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

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{15}H_9ClO_3$
M_r	272.67
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	173
a, *b*, *c* (Å)	13.267 (7), 5.1050 (18), 18.866 (9)
β (°)	109.67 (2)
V (Å^3)	1203.2 (10)
Z	4
Radiation type	Mo *K*α
μ (mm^{-1})	0.32
Crystal size (mm)	0.6 × 0.1 × 0.1
Data collection	
Diffractometer	Rigaku XtaLab mini with hybrid CCD photon counting detector
Absorption correction	Multi-scan (*REQAB*; Rigaku, 1998)
T_{min}, T_{max}	0.848, 1.00
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	12153, 2790, 1798
R_{int}	0.134
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.652
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.059, 0.148, 1.03
No. of reflections	2790
No. of parameters	176
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.25, −0.33

Computer programs: *CrystalClear-SM Expert* (Rigaku, 2011), *SHELXT* (Sheldrick, 2015*a*), *SHELXL2014* (Sheldrick, 2015*b*) and *OLEX2* (Dolomanov *et al.*, 2009).

Refinement

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

Acknowledgements

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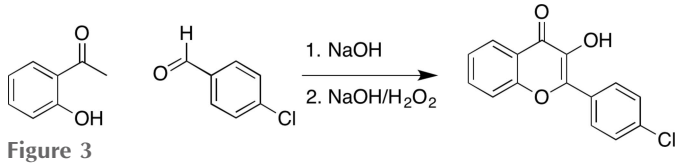

Figure 3
Reaction sequence for the synthesis of the title compound.

Kurzwernhart, A., Kandioller, W., Bächler, S., Bartel, C., Martic, S., Buczkowska, M., Mühlgassner, G., Jakupec, M., Kraatz, H.-B., Bednarski, P., Arion, V., Marko, D., Keppler, B. & Hartinger, C. (2012). *J. Med. Chem.* **55**, 10512–10522.
Rigaku (1998). *REQAB*. Rigaku Corporation, Tokyo, Japan.
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Sheldrick, G. M. (2015*a*). *Acta Cryst.* A**71**, 3–8.
Sheldrick, G. M. (2015*b*). *Acta Cryst.* C**71**, 3–8.

full crystallographic data

IUCrData (2017). **2**, x170996 [https://doi.org/10.1107/S2414314617009968]

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Crystal data

$C_{15}H_9ClO_3$
M_r = 272.67
Monoclinic, $P2_1/n$
a = 13.267 (7) Å
b = 5.1050 (18) Å
c = 18.866 (9) Å
β = 109.67 (2)°
V = 1203.2 (10) Å^3
Z = 4
$F(000)$ = 560
D_x = 1.505 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 2168 reflections
θ = 2.3–27.5°
μ = 0.32 mm^{-1}
T = 173 K
Prism, colorless
0.6 × 0.1 × 0.1 mm

Data collection

Rigaku XtaLab mini with hybrid CCD photon counting detector diffractometer
ω scans
Absorption correction: multi-scan (*REQAB*; Rigaku, 1998)
T_{min} = 0.848, T_{max} = 1.00
12153 measured reflections
2790 independent reflections
1798 reflections with $I > 2\sigma(I)$
R_{int} = 0.134
θ_{max} = 27.6°, θ_{min} = 1.7°
h = −17→17
k = −6→6
l = −24→24

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.059
$wR(F^2)$ = 0.148
S = 1.03
2790 reflections
176 parameters
0 restraints
Primary atom site location: dual
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.045P)^2 + 0.358P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.25 e Å^{-3}
$\Delta\rho_{min}$ = −0.33 e Å^{-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. All H atoms were positioned geometrically and refined as riding with C—H = 0.95 or 0.98 Å and U_{iso}(H) = 1.2U_{eq}(C) or U_{iso}(H) = 1.5U_{eq}(C) for C(H) and C(H,H,H) groups respectively. Positions and thermal parameters of hydroxyl H atoms were freely refined.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
Cl1	0.29231 (7)	−0.28855 (15)	0.31556 (4)	0.0465 (3)
O2	0.35505 (15)	0.5852 (4)	0.58662 (10)	0.0319 (5)
O3	0.07635 (17)	0.6574 (4)	0.46991 (12)	0.0378 (5)
O1	0.09468 (17)	1.0214 (4)	0.57933 (11)	0.0434 (6)
C4	0.3655 (2)	0.7714 (5)	0.64026 (15)	0.0299 (6)
C3	0.2581 (2)	0.5458 (5)	0.53041 (14)	0.0280 (6)
C10	0.2654 (2)	0.3419 (5)	0.47707 (15)	0.0288 (6)
C1	0.1756 (2)	0.8890 (6)	0.58247 (15)	0.0315 (6)
C5	0.2797 (2)	0.9286 (6)	0.64112 (14)	0.0299 (6)
C2	0.1711 (2)	0.6911 (5)	0.52714 (15)	0.0293 (6)
C11	0.1738 (2)	0.2221 (6)	0.42686 (15)	0.0332 (7)
H11	0.1064	0.2712	0.4271	0.040*
C9	0.2971 (2)	1.1185 (6)	0.69760 (16)	0.0361 (7)
H9	0.2409	1.2249	0.6990	0.043*
C12	0.1827 (2)	0.0323 (6)	0.37722 (15)	0.0358 (7)
H12	0.1215	−0.0439	0.3437	0.043*
C13	0.2827 (3)	−0.0442 (6)	0.37737 (15)	0.0349 (7)
C15	0.3655 (2)	0.2598 (6)	0.47606 (16)	0.0355 (7)
H15	0.4272	0.3355	0.5092	0.043*
C14	0.3744 (2)	0.0684 (6)	0.42671 (16)	0.0381 (7)
H14	0.4415	0.0156	0.4267	0.046*
C6	0.4670 (2)	0.8002 (6)	0.69450 (16)	0.0371 (7)
H6	0.5235	0.6941	0.6935	0.045*
C8	0.3977 (3)	1.1489 (6)	0.75141 (16)	0.0381 (7)
H8	0.4089	1.2760	0.7886	0.046*
C7	0.4821 (3)	0.9891 (6)	0.74977 (17)	0.0408 (8)
H7	0.5493	1.0096	0.7862	0.049*
H3	0.035 (4)	0.780 (9)	0.471 (3)	0.103 (18)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0659 (6)	0.0394 (4)	0.0341 (4)	0.0075 (4)	0.0166 (4)	−0.0049 (3)
O2	0.0270 (10)	0.0373 (11)	0.0264 (10)	0.0045 (9)	0.0023 (9)	−0.0038 (8)
O3	0.0256 (11)	0.0457 (13)	0.0364 (12)	0.0028 (10)	0.0030 (9)	−0.0071 (10)
O1	0.0338 (12)	0.0591 (14)	0.0347 (12)	0.0145 (11)	0.0083 (10)	−0.0065 (10)
C4	0.0327 (16)	0.0312 (14)	0.0249 (14)	0.0001 (12)	0.0085 (13)	−0.0015 (11)
C3	0.0265 (14)	0.0325 (15)	0.0212 (13)	0.0005 (12)	0.0032 (12)	0.0031 (11)
C10	0.0309 (15)	0.0289 (15)	0.0255 (14)	0.0020 (12)	0.0080 (12)	0.0047 (11)
C1	0.0305 (16)	0.0378 (16)	0.0276 (14)	0.0031 (13)	0.0115 (13)	0.0050 (12)
C5	0.0311 (15)	0.0357 (15)	0.0244 (14)	0.0007 (13)	0.0115 (13)	0.0022 (12)
C2	0.0277 (15)	0.0337 (15)	0.0258 (14)	−0.0013 (12)	0.0078 (12)	0.0001 (12)
C11	0.0315 (16)	0.0370 (16)	0.0276 (14)	0.0013 (13)	0.0052 (13)	0.0016 (12)
C9	0.0382 (17)	0.0383 (16)	0.0317 (15)	0.0000 (13)	0.0118 (14)	−0.0019 (12)
C12	0.0408 (18)	0.0350 (16)	0.0276 (15)	−0.0005 (13)	0.0061 (14)	−0.0017 (12)

C13	0.0492 (19)	0.0299 (15)	0.0240 (14)	0.0048 (14)	0.0103 (14)	0.0031 (11)
C15	0.0277 (15)	0.0403 (17)	0.0329 (15)	0.0054 (13)	0.0027 (13)	−0.0007 (13)
C14	0.0374 (17)	0.0427 (17)	0.0354 (17)	0.0094 (14)	0.0137 (15)	−0.0005 (14)
C6	0.0321 (16)	0.0422 (17)	0.0334 (16)	0.0025 (13)	0.0063 (14)	−0.0046 (13)
C8	0.0423 (18)	0.0400 (17)	0.0301 (15)	−0.0065 (14)	0.0096 (14)	−0.0076 (13)
C7	0.0367 (18)	0.0472 (18)	0.0324 (16)	−0.0041 (15)	0.0036 (14)	−0.0055 (14)

Geometric parameters (Å, º)

Cl1—C13	1.742 (3)	C11—H11	0.9300
O2—C4	1.361 (3)	C11—C12	1.380 (4)
O2—C3	1.379 (3)	C9—H9	0.9300
O3—C2	1.365 (3)	C9—C8	1.387 (4)
O3—H3	0.83 (5)	C12—H12	0.9300
O1—C1	1.252 (3)	C12—C13	1.381 (4)
C4—C5	1.398 (4)	C13—C14	1.384 (4)
C4—C6	1.398 (4)	C15—H15	0.9300
C3—C10	1.473 (4)	C15—C14	1.382 (4)
C3—C2	1.356 (4)	C14—H14	0.9300
C10—C11	1.405 (4)	C6—H6	0.9300
C10—C15	1.399 (4)	C6—C7	1.384 (4)
C1—C5	1.464 (4)	C8—H8	0.9300
C1—C2	1.440 (4)	C8—C7	1.394 (4)
C5—C9	1.401 (4)	C7—H7	0.9300
C4—O2—C3	120.6 (2)	C8—C9—C5	120.4 (3)
C2—O3—H3	109 (3)	C8—C9—H9	119.8
O2—C4—C5	122.0 (2)	C11—C12—H12	120.0
O2—C4—C6	116.7 (2)	C13—C12—C11	119.9 (3)
C5—C4—C6	121.3 (3)	C13—C12—H12	120.0
O2—C3—C10	111.7 (2)	C12—C13—Cl1	119.2 (2)
C2—C3—O2	121.0 (2)	C12—C13—C14	120.7 (3)
C2—C3—C10	127.3 (2)	C14—C13—Cl1	120.1 (2)
C11—C10—C3	121.8 (3)	C10—C15—H15	119.4
C15—C10—C3	120.1 (3)	C14—C15—C10	121.2 (3)
C15—C10—C11	118.1 (3)	C14—C15—H15	119.4
O1—C1—C5	122.5 (3)	C13—C14—H14	120.3
O1—C1—C2	121.3 (3)	C15—C14—C13	119.4 (3)
C2—C1—C5	116.3 (2)	C15—C14—H14	120.3
C4—C5—C1	118.5 (2)	C4—C6—H6	120.5
C4—C5—C9	118.6 (3)	C7—C6—C4	119.0 (3)
C9—C5—C1	122.9 (3)	C7—C6—H6	120.5
O3—C2—C1	117.6 (2)	C9—C8—H8	120.0
C3—C2—O3	120.7 (3)	C9—C8—C7	120.0 (3)
C3—C2—C1	121.7 (3)	C7—C8—H8	120.0
C10—C11—H11	119.6	C6—C7—C8	120.7 (3)
C12—C11—C10	120.7 (3)	C6—C7—H7	119.7
C12—C11—H11	119.6	C8—C7—H7	119.7

C5—C9—H9	119.8

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H3···O1^{i}	0.84 (5)	1.95 (5)	2.698 (3)	149 (4)

Symmetry code: (i) −*x*, −*y*+2, −*z*+1.