

3,3a-Dihydrocyclopenta[*b*]chromen-1(2*H*)-ones from the reaction of salicylaldehyde and 2-cyclopenten-1-one

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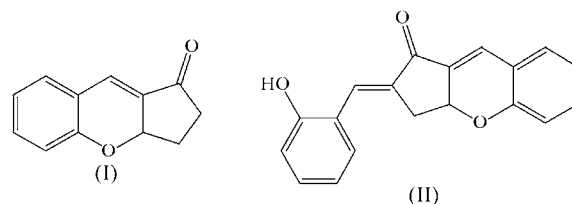
The two title chromene compounds, 3,3a-dihydrocyclopenta[*b*]chromen-1(2*H*)-one, C₁₆H₁₂O₂, (I), and 2-(2-hydroxybenzylidene)-3,3a-dihydrocyclopenta[*b*]chromen-1(2*H*)-one, C₁₉H₁₄O₃, (II), have been determined in the monoclinic space group *P*2₁/*n*. Compound (I) is mainly stabilized by C—H··· π interactions. Compound (II) is linked into infinite one-dimensional chains with a *C*(3) motif *via* intermolecular O—H···O hydrogen bonds. The intermolecular C—H··· π and π — π interactions also play key roles in stabilizing the crystal packing. Two intramolecular C—H···O hydrogen bonds with *S*(5) motifs were detected in (II).

Comment

Chromenes (2*H*-1-benzopyran derivatives) are frequently found in naturally occurring heterocycles, many of which exhibit biological activity (Bowers *et al.*, 1976) and have been widely employed as important intermediates in the synthesis of natural products and medicinal agents (Wang & Finn, 2000). Thus, various synthetic methods for the formation of these compounds have been reported (Kaye & Nocanda, 2000; Parker & Mindt, 2001).

Most recently, the reaction of 2-hydroxybenzaldehyde and cyclopenten-2-one, a typical Baylis–Hillman coupling, was suggested to occur through a domino oxa-Michael addition/aldol condensation pathway in the presence of DMAP (dimethylaminopyridine; Lee *et al.*, 2003) or DABCO (diazabicyclo[2.2.2]octane; Bräse & Lesch, 2004) under aqueous conditions. We have also carried out the reactions with imidazole as a catalyst. Several crystal structures of chromene derivatives have been published (Huo *et al.*, 2004*a,b,c*). In the present paper, another two crystal structures are reported, namely 3,3a-dihydrocyclopenta[*b*]chromen-1(2*H*)-one, (I), and 2-(2-hydroxybenzylidene)-3,3a-dihydrocyclopenta[*b*]chromen-1(2*H*)-one, (II).

In the five derivatives that we have studied, [7*a*,8,9,10-tetrahydrobenzo[*f*]cyclopenta[*b*]chromen-10-one (Huo *et al.*, 2004*a*), 7-nitro- and 7-methoxy-2,3-dihydro-1*H*-cyclopenta[*b*]chromen-1-one (Huo *et al.*, 2004*b,c*), and the title compounds (I) and (II), similarities in the geometry are observed and the pyran ring has the same configuration (*i.e.* half-chair). However, the crystal packings of the five compounds differ, partly because of the presence of different substituents.



Selected geometric parameters of (I) are listed in Table 1 and an ellipsoid plot of the molecule is shown in Fig. 1. X-ray analysis of the good quality single crystals obtained revealed a

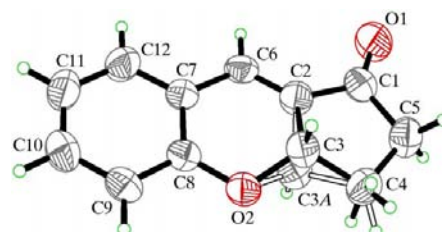


Figure 1
A view of the molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. The suffix *A* denotes the 41% minor disorder component.

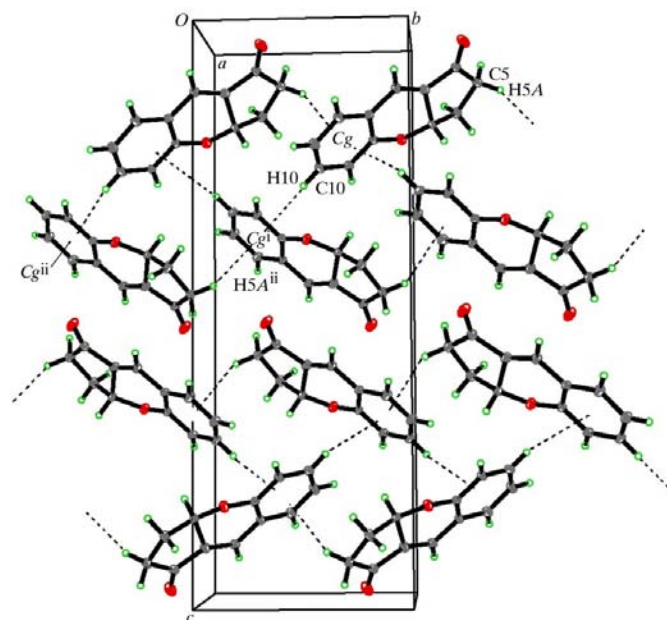


Figure 2
The packing of (I), viewed down the *a* axis. C—H···*C*_g interactions are indicated by dashed lines. The minor component of the disorder has been omitted for clarity. [Symmetry codes: (i) $\frac{3}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$; (ii) $\frac{3}{2} - x, y - \frac{3}{2}, \frac{1}{2} - z$.]

monoclinic crystal lattice with the $P2_1/n$ space group. Atom C3 of the pyran ring is disordered over two sites, with a ratio of 0.59 (6):0.41 (6) for the major and minor components, respectively. All atoms, except atom C3, are coplanar within ± 0.0611 (2) Å, while atom C3 deviates from the plane of the other ring atoms by 0.4784 (3) Å. The pyran ring adopts a half-chair conformation, the dihedral angle between the O2/C3/C2 and O2/C8/C7/C6 planes being 38.02 (2)°. The C1–C2–C3–O2 and C6–C2–C3–O2 torsion angles are -152.7 (2) and 40.2 (3)°, respectively. For the minor component, the C1–C2–C3A–O2 and C6–C2–C3A–O2 torsion angles are 156.0 (2) and -43.2 (3)°, respectively. The packing of the crystals indicates that the adjacent molecules show two C–H $\cdots\pi$ (edge-to-face) interactions, elucidated by PLATON (Spek, 2003), with the π system of the C7–C12 ring (with centroid Cg; Fig. 2). In the first of these interactions, cyclopentene ring atom C5 interacts with Cg at (x , $1 + y$, z)

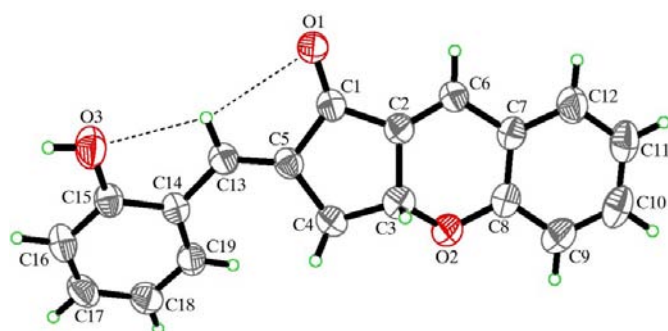


Figure 3
A view of the molecular structure of (II). Displacement ellipsoids are shown at the 50% probability level. The intramolecular hydrogen bonds are indicated by dashed lines.

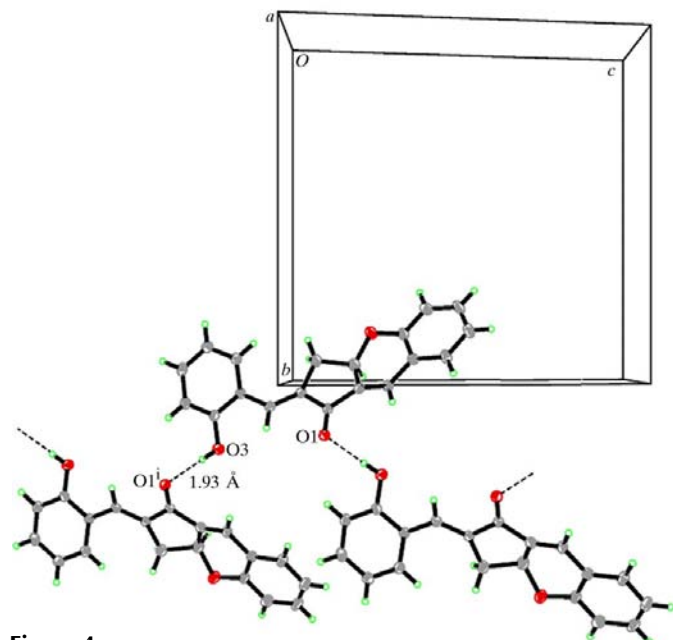


Figure 4
The packing of (II). Infinite one-dimensional O–H \cdots O hydrogen-bonded chains along the [101] orientation are indicated by dashed lines. The view is down the a axis. [Symmetry code: (i) $x - \frac{1}{2}$, $-y + \frac{5}{2}$, $z - \frac{1}{2}$]

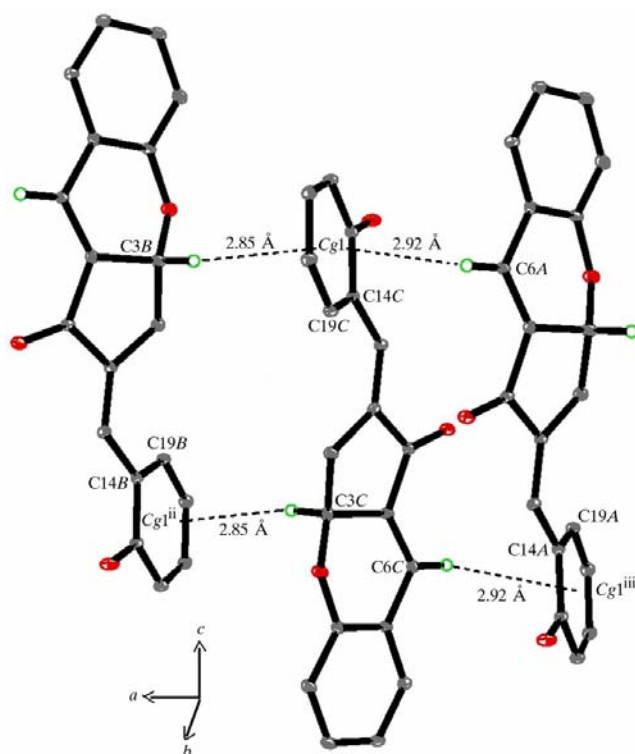


Figure 5
The C6–H6 \cdots Cg1ⁱⁱ and C3–H3 \cdots Cg1ⁱⁱⁱ [symmetry codes: (ii) $-x + 2$, $-y + 2$, $-z$; (iii) $-x + 1$, $-y + 2$, $-z$; Cg1 is the centroid of the C14–C19 ring] interactions in the structure of (II). Selected atoms are labeled. H atoms, except for atoms H3 and H6, have been omitted for clarity.

[C5 \cdots Cg = 3.776 (2) Å, H5A \cdots Cg = 2.89 Å and C5–H5A \cdots Cg = 153°]. In the second interaction, benzene atom C10 interacts with Cg at ($\frac{3}{2} - x$, $-\frac{1}{2} + y$, $\frac{1}{2} - z$) [C10 \cdots Cg = 3.901 (2) Å, H10 \cdots Cg = 3.22 Å and C10–H10 \cdots Cg = 132°]. Selected geometric parameters of (II) are listed in Table 2 and an ellipsoid plot of the molecule is shown in Fig. 3. Single-crystal X-ray analysis of the crystals of (II) revealed a monoclinic crystal lattice with the $P2_1/n$ space group. The chromene fragment of the molecule is the same as that of (I). Except for atom C3, all atoms are coplanar within ± 0.187 (2) Å, with atom C3 deviating by 0.4051 (2) Å. The dihedral angle between the O2/C3/C2 and O2/C8/C7/C6 planes is 35.51 (2)°. The C1–C2–C3–O2 and C6–C2–C3–C4 torsion angles are 146.9 (2) and -151.0 (2)°, respectively. The C14–C19 benzene ring and the chromene fragment are joined by atom C13. The C14–C13–C5–C4 and C5–C13–C14–C19 torsion angles are -5.6 (3) and -23.4 (3)°. A linear O–H \cdots O intermolecular hydrogen bond of the hydroxy group was observed in the crystal structure of (II) (Fig. 4). This strong interaction links the molecules into an infinite one-dimensional chain along [101], with a $C(3)$ motif (Bernstein *et al.*, 1995). The hydrogen-bonding parameters include an H1 \cdots O1 distance of 1.93 Å and an O3–H1 \cdots O1 angle of 178° (Table 3). Further analysis indicates that the crystal has two intramolecular C–H \cdots O hydrogen bonds (Table 3), with the sp^2 C13 atom acting as the only donor, and the carbonyl and hydroxy O atoms acting as acceptors. The O1 \cdots H13 \cdots O3 angle is 153°. Furthermore, three inter-

molecular C—H... π interactions (Table 3; *Cg1* is the centroid of the C14–C19 ring and *Cg2* the centroid of the C7–C12 ring) and π – π interactions are detected, which stabilize the crystal stacking. Fig. 5 shows the two C—H... π (edge-to-face) interactions related to the π electrons of the C14–C19 benzene ring (with centroid *Cg1*).

Experimental

The title compounds were synthesized by Baylis–Hillman reactions. At room temperature, a clear solution of 2-hydroxybenzaldehyde (1 mmol), cyclopenten-2-one (2 mmol) and imidazole (1 mmol) in tetrahydrofuran (1.5 ml) was mixed with deionized water (1.5 ml). The mixture was stirred at ambient temperature for 48 h to complete the reaction. The mixture was diluted with water (10 ml) and extracted with ethyl acetate. The organic layer was concentrated under reduced pressure. After the usual work-up, chromatography of the crude product on silica gel, using ethyl acetate and petroleum ether (1:4) as eluant, gave pure (I) in a yield of 53% and a little (II). Compound (I) (60 mg) was dissolved in CHCl₃ (2 ml). The solution was allowed to evaporate slowly at room temperature for several days. Yellow crystals suitable for X-ray analysis were formed. Crystals of (II) were formed during chromatography processes.

Compound (I)

Crystal data

C₁₂H₁₀O₂ *D_x* = 1.353 Mg m⁻³
M_r = 186.20 Mo *K* α radiation
 Monoclinic, *P*2₁/*n* Cell parameters from 4188 reflections
a = 5.8015 (14) Å θ = 2.9–26.9°
b = 7.6260 (19) Å μ = 0.09 mm⁻¹
c = 20.661 (5) Å *T* = 298 (2) K
 β = 91.254 (3)° Block, yellow
V = 913.9 (4) Å³ 0.73 × 0.25 × 0.25 mm
Z = 4

Data collection

Bruker SMART CCD area-detector 1579 independent reflections
 diffractometer 1324 reflections with *I* > 2 σ (*I*)
 ω scans *R*_{int} = 0.016
 Absorption correction: multi-scan θ _{max} = 25.0°
 (SADABS; Sheldrick, 1996) *h* = -6 → 5
*T*_{min} = 0.723, *T*_{max} = 0.978 *k* = -8 → 9
 4188 measured reflections *l* = -21 → 24

Refinement

Refinement on *F*² $w = 1/[\sigma^2(F_o^2) + (0.0656P)^2 + 0.2252P]$
 $R[F^2 > 2\sigma(F^2)] = 0.046$ where $P = (F_o^2 + 2F_c^2)/3$
 $wR(F^2) = 0.126$ (Δ/σ)_{max} < 0.001
S = 1.04 $\Delta\rho$ _{max} = 0.24 e Å⁻³
 1579 reflections $\Delta\rho$ _{min} = -0.22 e Å⁻³
 137 parameters
 H-atom parameters constrained

Table 1

Selected geometric parameters (Å, °) for (I).

| | | | |
|-------------|--------------|--------------|-------------|
| O2–C3A | 1.408 (3) | C2–C3A | 1.544 (3) |
| O2–C3 | 1.415 (3) | C3–C4 | 1.493 (3) |
| C2–C6 | 1.312 (2) | C3A–C4 | 1.490 (3) |
| C2–C3 | 1.534 (3) | | |
| C6–C2–C1 | 132.68 (16) | C2–C6–C7 | 119.51 (15) |
| C6–C2–C3–O2 | 40.2 (3) | C6–C2–C3A–O2 | -43.2 (3) |
| C1–C2–C3–O2 | -152.68 (18) | C1–C2–C3A–O2 | 156.04 (19) |

Compound (II)

Crystal data

C₁₉H₁₄O₃ *D_x* = 1.336 Mg m⁻³
M_r = 290.30 Mo *K* α radiation
 Monoclinic, *P*2₁/*n* Cell parameters from 5951 reflections
a = 8.8978 (9) Å θ = 2.3–24.6°
b = 12.5893 (12) Å μ = 0.09 mm⁻¹
c = 13.1797 (13) Å *T* = 298 (2) K
 β = 102.157 (2)° Block, orange
V = 1443.2 (2) Å³ 0.36 × 0.23 × 0.23 mm
Z = 4

Data collection

Bruker SMART CCD area-detector 1881 reflections with *I* > 2 σ (*I*)
 diffractometer *R*_{int} = 0.056
 ω scans θ _{max} = 25.0°
 Absorption correction: multi-scan *h* = -10 → 10
 (SADABS; Sheldrick, 1996) *k* = -13 → 14
*T*_{min} = 0.733, *T*_{max} = 0.980 *l* = -15 → 12
 5951 measured reflections
 2543 independent reflections

Refinement

Refinement on *F*² $w = 1/[\sigma^2(F_o^2) + (0.0745P)^2]$
 $R[F^2 > 2\sigma(F^2)] = 0.051$ where $P = (F_o^2 + 2F_c^2)/3$
 $wR(F^2) = 0.135$ (Δ/σ)_{max} < 0.001
S = 1.00 $\Delta\rho$ _{max} = 0.43 e Å⁻³
 2543 reflections $\Delta\rho$ _{min} = -0.17 e Å⁻³
 200 parameters
 H-atom parameters constrained

Table 2

Selected geometric parameters (Å, °) for (II).

| | | | |
|----------------|-------------|-------------|-------------|
| O2–C8 | 1.372 (2) | C6–C7 | 1.446 (3) |
| O2–C3 | 1.422 (3) | C13–C5 | 1.335 (3) |
| C6–C2 | 1.327 (3) | C13–C14 | 1.460 (3) |
| C2–C6–C7 | 118.87 (18) | C13–C5–C1 | 121.93 (17) |
| C5–C13–C14 | 129.32 (19) | C13–C5–C4 | 129.92 (17) |
| C6–C2–C1 | 130.69 (18) | | |
| C5–C13–C14–C19 | -23.4 (3) | C1–C2–C3–O2 | 146.85 (17) |
| C14–C13–C5–C4 | -5.6 (3) | C6–C2–C3–C4 | -151.0 (2) |

Table 3

Hydrogen-bond geometry (Å, °) for (II).

Cg1 and *Cg2* are the centroids of the C14–C19 and C7–C12 benzene rings, respectively.

| <i>D</i> –H... <i>A</i> | <i>D</i> –H | H... <i>A</i> | <i>D</i> ... <i>A</i> | <i>D</i> –H... <i>A</i> |
|-------------------------------------|-------------|---------------|-----------------------|-------------------------|
| C13–H13...O3 | 0.93 | 2.42 | 2.750 (2) | 101 |
| C13–H13...O1 | 0.93 | 2.59 | 2.917 (2) | 102 |
| O3–H1...O1 ⁱ | 0.82 | 1.93 | 2.749 (2) | 178 |
| C3–H3... <i>Cg1</i> ⁱⁱⁱ | 0.98 | 2.85 | 3.746 (2) | 152 |
| C6–H6... <i>Cg1</i> ⁱⁱ | 0.93 | 2.92 | 3.476 (2) | 120 |
| C12–H12... <i>Cg2</i> ^{iv} | 0.93 | 3.25 | 3.471 (2) | 96 |

Symmetry codes: (i) $x - \frac{1}{2}, -y + \frac{5}{2}, z - \frac{1}{2}$; (ii) $-x + 2, -y + 2, -z$; (iii) $-x + 1, -y + 2, -z$; (iv) $-x + 2, -y + 2, -z + 1$.

All H atoms were placed in calculated positions and allowed to ride on their parent atoms, with *U*_{iso}(H) values set at 1.5*U*_{eq}(parent atom) for the *Csp*³-bound H atoms and the hydroxy-group O atom, and 1.2*U*_{eq}(parent atom) for *Csp*²-bound H atoms. The C–H distances were fixed in the range 0.93–0.98 Å and O–H distances were fixed at 0.82 Å.

For both compounds, data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2000); software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1811). Services for accessing these data are described at the back of the journal.

References

- Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
- Bowers, R. S., Ohta, T., Cleere, J. S. & Marsella, P. A. (1976). *Science*, **193**, 542–547.
- Bräse, S. & Lesch, B. (2004). *Angew. Chem. Int. Ed.* **43**, 115–118.
- Bruker (2000). *SMART* (Version 5.0), *SAINT* (Version 6.02) and *SHELXTL* (Version 6.1). Bruker AXS Inc., Madison, Wisconsin, USA.
- Huo, F. J., Yin, C. X. & Yang, P. (2004a). *Acta Cryst.* **E60**, o1671–o1673.
- Huo, F. J., Yin, C. X. & Yang, P. (2004b). *Acta Cryst.* **E60**, o2087–o2089.
- Huo, F. J., Yin, C. X. & Yang, P. (2004c). *Acta Cryst.* **E60**, o2278–o2280.
- Kaye, P. T. & Nocanda, X. W. (2000). *J. Chem. Soc. Perkin Trans. 1*, pp. 1331–1332.
- Lee, K. Y., Kim, J. M. & Kim, J. N. (2003). *Bull. Korean Chem. Soc.* **24**, 17–18.
- Parker, K. A. & Mindt, T. L. (2001). *Org. Lett.* **3**, 3875–3878.
- Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
- Sheldrick, G. M. (1997). *SHELXL97* and *SHELXS97*. University of Göttingen, Germany.
- Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.
- Wang, Q. & Finn, M. G. (2000). *Org. Lett.* **2**, 4063–4065.