3,3a-Dihydrocyclopenta[b]chromen-1(2H)-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(2H)-one, C10H12O2, (I), and 2-(2-hydroxybenzylidene)-3,3a-dihydrocyclopenta[b]chromen-1(2H)-one, C10H12O2, (II), have been determined in the monoclinic space group P21/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 (2H-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 (diaza-bicyclo[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., 2004a,b,c). In the present paper, another two crystal structures are reported, namely 3,3a-dihydrocyclopenta[b]chromen-1(2H)-one, (I), and 2-(2-hydroxybenzylidene)-3,3a-dihydrocyclopenta[b]chromen-1(2H)-one, (II).

In the five derivatives that we have studied, [7a,8,9,10-tetrahydrobenz[f]cyclopenta[b]chromen-10-one (Huo et al., 2004a), 7-nitro- and 7-methoxy-2,3-dihydro-1H-cyclopenta[b]chromen-1-one (Huo et al., 2004b,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
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 $\pm 0.0611$ (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)$^\circ$. The C1–C2–C3–O2 and C6–C2–C3–O2 torsion angles are $-152.7$ (2) and 40.2 (3)$^\circ$, 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)$^\circ$, respectively. The packing of the crystals indicates that the adjacent molecules show two C–H···π (edge-to-face) interactions, elucidated by PLATON (Spek, 2003), with the π system of the C7–C12 ring (with centroid $C_g$; Fig. 2). In the first of these interactions, cyclopentene ring atom C5 interacts with $C_g$ at $(x, 1 + y, z)$

$$[C5\cdots C_g = 3.776$ (2) Å, $H5A\cdots C_g = 2.89$ Å and $C5–H5A\cdots C_g = 153\^\circ]$ In the second interaction, benzene atom C10 interacts with $C_g$ at $(\frac{1}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z)$ [C10–Cg = 3.901 (2) Å, H10–Cg = 3.22 Å and C10–H10–Cg = 132\^\circ]. 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 $\pm 0.187$ (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)$^\circ$. The C1–C2–C3–O2 and C6–C2–C3–C4 torsion angles are 146.9 (2) and $-151.0$ (2)$^\circ$, 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)$^\circ$. A linear O–H···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–O1 distance of 1.93 Å and an O3–H1–O1 angle of 178° (Table 3). Further analysis indicates that the crystal has two intramolecular C–H···O hydrogen bonds (Table 3), with the sp$^2$ C3 atom acting as the only donor, and the carbonyl and hydroxy O atoms acting as acceptors. The O1–H13···O3 angle is 153°. Furthermore, three inter-

**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···O hydrogen-bonded chains along the [101] orientation are indicated by dashed lines. The view is down the a axis [Symmetry code: (i) $x, -\frac{1}{2} - y, \frac{1}{2} - z$]
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), cyclopentene-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  
M₁ = 186.20  
Monoclinic, P2₁/n  
α = 5.8015 (14) Å  
β = 91.254 (3) Å  
V = 913.9 (4) Å³  
Z = 4  
Mo Kα radiation  
Cell parameters from 4188 reflections  
θ = 2.9–26.9°  
μ = 0.09 mm⁻¹  
T = 298 (2) K  
Block, yellow  
0.73 × 0.25 × 0.25 mm

**Data collection**

Bruker SMART CCD area-detector diffractometer  
1579 independent reflections  
1324 reflections with I > 2 σ(I)  
Rint = 0.016  
Absorption correction: multi-scans  
(SADABS; Sheldrick, 1996)  
h = −9 → 9  
k = −8 → 9  
l = −21 → 24

**Refinement**

Refinement on F²  
R[F² > 2σ(F²)] = 0.046  
wR(F²) = 0.126  
S = 1.04  
1579 reflections  
137 parameters  
H-atom parameters constrained

**Table 1**

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

|  | C2–C3 | 1.415 (3) | C3–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) |

**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 | 118.97 (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).

|  | D–H · · · A | D–H | H · · · A | D · · A | D–H · · · A |
|  | C13–H13–O3 | 0.93 | 2.42 | 2.70 (2) | 101 |
|  | C13–H13–O1 | 0.93 | 2.59 | 2.917 (2) | 102 |
|  | O3–H1–O1 | 0.82 | 1.93 | 2.749 (2) | 178 |
|  | C3–H3–C11 | 0.98 | 2.85 | 3.746 (2) | 152 |
|  | C6–H6–C11 | 0.93 | 2.92 | 3.476 (2) | 120 |
|  | C12–H12–C20v | 0.93 | 3.25 | 3.471 (2) | 96 |

Symmetry codes: (i) x−1, y−1, z−1; (ii) −x+2, −y+2, −z−1; (iii) −x−1, −y−1, −z−1; (iv) −x+2, −y+2, −z+1.

All H atoms were placed in calculated positions and allowed to ride on their parent atoms, with Uiso(H) values set at 1.2Ueq(parent atom) for the Csp³-bound H atoms and the hydrogen-group O atom, and 1.2Ueq(pivot) for Csp²-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: SAIN T (Bruker, 2000); data reduction: SAIN T; 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