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5-Chloro-2-hydroxybenzophenone, featuring O—H···O, C—H···O, C—H···π and π–π interactions

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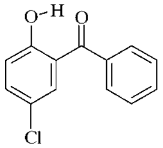
Molecules of the title compound, $C_{13}H_9ClO_2$, contain an intramolecular O—H···O hydrogen bond, and the two aromatic rings are inclined at 57.02 (3)° with respect to one another. The crystal structure is supported by C—H···O, C—H···π and π–π interactions.

Comment

The title compound, (I), also known as benzophenone-7, is a UV light absorber that has been found in cosmetics and personal-care products (Health Canada, 2002). Related molecules, *e.g.* benzophenones-1, -2, -3, -4, -6, -8 and -12 (Wang & Lee, 2003), are used as sunscreeen agents. The crystal structures of chlorinated benzophenones, such as 4-chloro-2-(3,4,5-trimethoxybenzoyl)phenol (Hsieh *et al.*, 2003) and pestalone (Cueto *et al.*, 2001), have also been determined and their role as potential anticancer agents and antibiotics has been examined.



(I)

In (I), the bond lengths and valence angles are normal and the molecular conformation can be characterized by the dihedral angle of 57.02 (3)° between the mean planes of the two aromatic rings. This compares with the value of 56° for benzophenone (Fleischer *et al.*, 1968) and 54.39 (8)° for 2-methylamino-5-chlorobenzophenone (Cox *et al.*, 1997). Another indicator of conformation are the values of the C2—C1—C7—O2 [10.5 (2)°] and C9—C8—C7—O2 [46.4 (2)°] torsion angles. For benzophenones, these torsion angles normally take the same sign and are each reported to be 30° in energy-minimized benzophenone (Rappoport *et al.*, 1990).

In (I), the carbonyl group at C7 and the hydroxy group at C2 are linked by an intramolecular hydrogen bond (Fig. 1 and Table 2). The resultant six-membered ring has a flattened twisted-boat conformation, with $^0S_2$ = 0.163 (Berces *et al.*, 2001). The O—H···O angle of 150 (2)° in (I) compares with the N—H···O angle of 133.1 (6)° in 2-methylamino-5-chlorobenzophenone (Cox *et al.*, 1997).

The supramolecular structure of (I) contains a weak intermolecular C6—H6···O1^i hydrogen bond [Table 2; symmetry code: (i) $x, \frac{1}{2} - y, \frac{1}{2} + z$]. The shortest Cl1···Cl1^{ii} contact of 3.5159 (6) Å [symmetry code: (ii) $-x, -1 - y, -z$] is comparable with the sum of the van der Waals radii (3.50 Å; Bondi, 1964). Fig. 2 indicates the O—H···O, C—H···O, C—H···π and π–π interactions. Here, C12—H12 = 0.96 (2) Å, H12···*Cg*2 = 2.82 (2) Å, C12—H12···*Cg*2 = 129 (1)° and

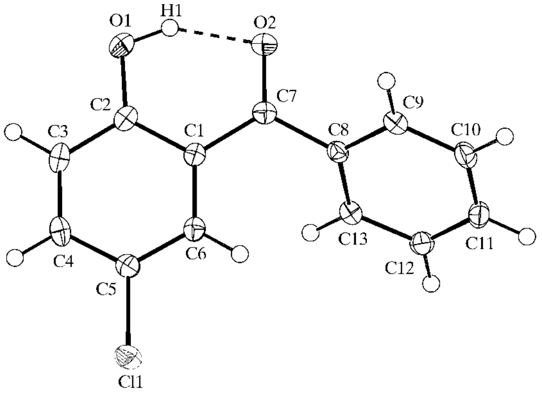


Figure 1
The atomic arrangement and atom labelling for the molecule of (I). Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. The intramolecular O—H···O interaction is shown as a broken line.

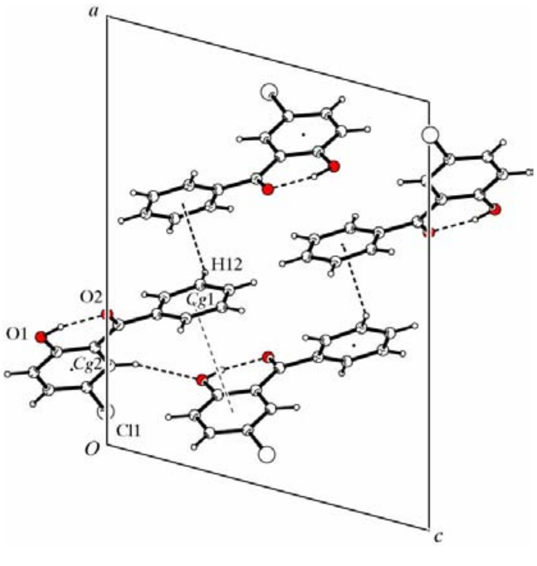


Figure 2
A partial packing diagram for (I), showing the O—H···O, C—H···O, C—H···π and π–π interactions as dotted lines. Ring centroids (*Cg*1 and *Cg*2) are indicated by isolated dots where the interactions are with other molecules.

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C12$\cdots$$Cg$2 = 3.505 (2) Å, where Cg2 is the centroid of the chlorohydroxy aromatic ring. The π–π interactions are between the phenyl ring and the chlorohydroxy aromatic ring, the latter being transposed by ($x, \frac{1}{2} - y, z - \frac{1}{2}$). Here, $Cg\cdots Cg$ is 4.2140 (9) Å, the dihedral angle is 10.5°, the interplanar distance is 3.702 (1) Å and the offset is 2.01 Å.

Crystal structures of related compounds include those of 2-(5′-chloro-2′-hydroxybenzoyl)benzoic acid (Skrzat, 1980), 2-amino-5-chlorobenzophenone (Vasco-Mendez *et al.*, 1996) and 4-amino-3-chlorobenzophenone (Lee *et al.*, 1994).

Experimental

The sample was purchased from Sigma and recrystallized from water.

Crystal data

$C_{13}H_9ClO_2$
M_r = 232.65
Monoclinic, $P2_1/c$
a = 15.3857 (3) Å
b = 5.8668 (1) Å
c = 11.9540 (3) Å
β = 104.985 (2)°
V = 1042.33 (12) Å^3
Z = 4
D_x = 1.483 Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 7838 reflections
θ = 2.9–27.5°
μ = 0.35 mm^{-1}
T = 120 (2) K
Square prism, yellow
0.2 × 0.1 × 0.1 mm

Data collection

Nonius KappaCCD area-detector diffractometer
φ and ω scans to fill the Ewald sphere
Absorption correction: multi-scan (*SORTAV*; Blessing, 1995, 1997)
$T_{\min}$ = 0.877, $T_{\max}$ = 0.970
12 435 measured reflections

2375 independent reflections
2133 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.069
$\theta_{\max}$ = 27.5°
$h = -19 \rightarrow 19$
$k = -7 \rightarrow 7$
$l = -15 \rightarrow 15$

Table 1
Selected geometric parameters (Å, °).

Cl1—C5	1.7435 (13)	O2—C7	1.2392 (16)
O1—C2	1.3506 (16)		
O1—C2—C1	122.10 (12)	O2—C7—C8	118.00 (11)
C7—C1—C2—O1	−2.02 (18)	O2—C7—C8—C13	−129.39 (13)
C6—C1—C7—O2	−166.75 (12)	O2—C7—C8—C9	46.36 (16)
C2—C1—C7—O2	10.52 (18)	C1—C7—C8—C9	−133.59 (13)

Table 2
Hydrogen-bonding geometry (Å, °).

D—H$\cdots$$A$	D—H	H$\cdots$$A$	$D\cdots A$	D—H$\cdots$$A$
O1—H1$\cdots$O2	0.92 (2)	1.73 (2)	2.571 (1)	150 (2)
C6—H6$\cdots$O1$^{\rm i}$	0.95 (2)	2.49 (2)	3.411 (2)	164 (2)

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

Refinement

Refinement on F^2
$R(F)$ = 0.034
$wR(F^2)$ = 0.092
S = 1.03
2375 reflections
182 parameters
All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.046P)^2 + 0.455P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max}$ = 0.31 e Å^{-3}
$\Delta\rho_{\min}$ = −0.29 e Å^{-3}

The H atoms were initially placed in calculated positions and thereafter allowed to refine freely [C—H = 0.948 (18)–0.969 (18) Å] with individual isotropic displacement parameters.

Data collection: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT* (Nonius, 1998); cell refinement: *DENZO* and *COLLECT*; data reduction: *DENZO* and *COLLECT*; program(s) used to solve structure: *SIR*97 (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2002); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1540). Services for accessing these data are described at the back of the journal.

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