

## A monohydrate pseudopolymorph of 3,4-dihydroxybenzophenone and the role of water in the crystal assembly of benzophenones

I. M. R. Landre,<sup>a</sup> T. E. Souza,<sup>a</sup> R. S. Corrêa,<sup>b</sup> F. T. Martins<sup>b</sup>  
and A. C. Doriguetto<sup>a\*</sup>

<sup>a</sup>Instituto de Ciências Exatas, Universidade Federal de Alfenas (UNIFAL–MG), Alfenas MG 37130-000, Brazil, and <sup>b</sup>Instituto de Física de São Carlos, Universidade de São Paulo, São Carlos SP 13560-970, Brazil  
Correspondence e-mail: doriguetto@unifal-mg.edu.br

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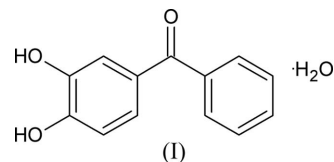
During a polymorphism screening of hydroxybenzophenone derivatives, a monohydrate pseudopolymorph of (3,4-dihydroxyphenyl)(phenyl)methanone, C<sub>13</sub>H<sub>10</sub>O<sub>3</sub>·H<sub>2</sub>O, (I), was obtained. Structural relationships and the role of water in crystal assembly were established on the basis of the known anhydrous form [Cox, Kechagias & Kelly (2008). *Acta Cryst. B* **64**, 206–216]. The crystal packing of (I) is stabilized by classical intermolecular O–H···O hydrogen bonds, generating a three-dimensional network.

### Comment

As part of our ongoing studies of polymorphism in molecular compounds and pharmaceuticals (Martins, Doriguetto & Ellena, 2010; Martins, Legendre *et al.*, 2010; Martins, Bocelli *et al.*, 2009; Martins, Papparidis *et al.* 2009; Corrêa *et al.*, 2006; Doriguetto *et al.*, 2004), we have studied 3,4-dihydroxybenzophenone, a synthetic hydroxybenzophenone. Hydroxybenzophenones have absorption bands in the near-UV and they are found in sun-protecting compounds in a variety of plastics and synthetic fabrics (Furukawa *et al.*, 1995; Ito *et al.*, 1994; Onishi *et al.*, 1987). Anti-inflammatory and antioxidant activities have also been reported for hydroxybenzophenone derivatives (Doriguetto *et al.*, 2007).

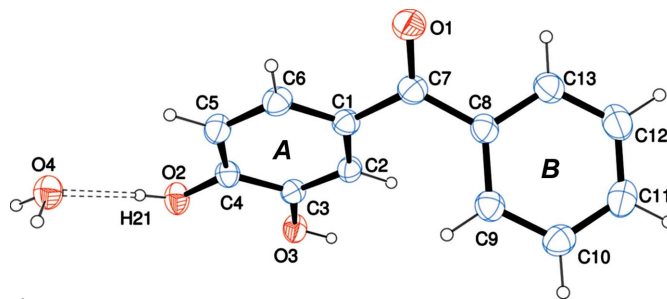
The structure of 3,4-dihydroxybenzophenone has been determined in its anhydrous form, (II), by X-ray diffraction analysis (Cox *et al.*, 2008). It crystallizes in the space group *C2/c*, with cell parameters  $a = 24.4619$  (9) Å,  $b = 7.3737$  (2) Å,  $c = 12.3961$  (4) Å and  $\beta = 115.019$  (2)°. In the present study, a new *P2<sub>1</sub>/n* monoclinic pseudopolymorph was found, the title monohydrate, (I) (Fig. 1). An overlay of the molecular backbones in both the anhydrous and the hydrated forms of 3,4-dihydroxybenzophenone clearly shows the conformational similarity between these structures. The r.m.s. deviation

between analogous non-H atoms is 0.0891 Å (Fig. 2). Thus, the two compounds do not show conformational differences but only packing changes as a consequence of water inclusion.

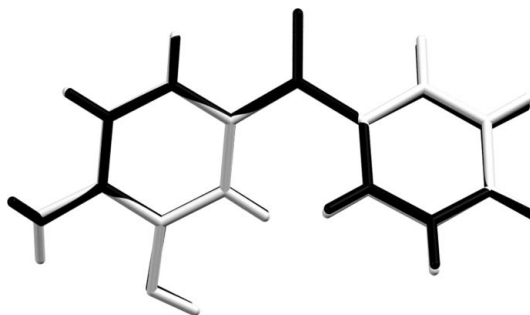


In terms of intramolecular geometry, the main difference between the anhydrous and hydrated forms is in the position of the hydroxy H atoms. In the monohydrate form, (I), there is no intramolecular hydrogen bonding between atoms O2 and O3 (Fig. 1). On the other hand, in the anhydrous form, (II), the H atom on atom O2 is localized between atoms O2 and O1 (Fig. 2), resulting in an intramolecular O2–H2···O1 hydrogen bond with O···O = 2.6391 (17) Å and O–H···O = 172 (2)°.

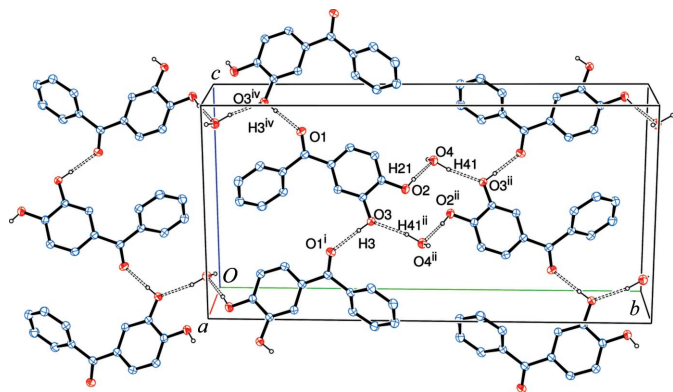
In the monohydrate, the least-squares planes through rings A and B (Fig. 1) form an angle of 56.3 (4)°, compared with an angle of 49.84 (5)° in the anhydrous form. The similar torsion angles between rings A and B suggest that this feature is related to hindrance effects involving these two rings. In the course of the intramolecular analysis, the geometric parameters of monohydrate (I) were analysed using the *Mogul* software (Bruno *et al.*, 2004). All geometric values agree with those of other reported hydroxybenzophenone structures (*e.g.* Cox *et al.*, 2008; Doriguetto *et al.*, 2007; Okabe & Kyoyama, 2002; Ferguson & Glidewell, 1996).



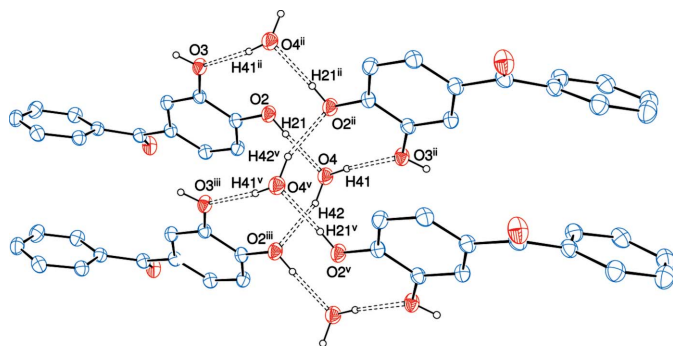
**Figure 1**  
The molecular structure of monohydrate (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.



**Figure 2**  
A superimposition of the monohydrated (black) and anhydrous (grey) forms of 3,4-dihydroxybenzophenone.

**Figure 3**

The crystal packing of (I), projected on to (101). Hydrogen bonds are shown as dashed lines. [Symmetry codes: (i)  $x + \frac{1}{2}, -y + \frac{1}{2}, z - \frac{1}{2}$ ; (ii)  $-x + 1, -y + 1, -z + 1$ ; (iv)  $x - \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2}$ ]

**Figure 4**

The crystal packing of (I), showing the role of water in the stabilization of the packing. Hydrogen bonds are shown as dashed lines. [Symmetry codes: (ii)  $-x + 1, -y + 1, -z + 1$ ; (iii)  $x - 1, y, z$ ; (v)  $-x, -y + 1, -z + 1$ .]

The supramolecular analysis of monohydrate (I) shows that there are four classical hydrogen bonds involving the hydroxy and carbonyl groups and the water molecule, contributing to the stabilization of the crystal packing (Figs. 3 and 4, and Table 1). *n*-Glide-related molecules are linked by O—H...O hydrogen bonds in which the hydroxy and carbonyl groups are involved as hydrogen-bonding donors and acceptors, respectively. Thus, the hydroxy O3—H3 group in the *meta* position is a hydrogen-bond donor to carbonyl atom O1<sup>i</sup> [symmetry code: (i)  $x + \frac{1}{2}, -y + \frac{1}{2}, z - \frac{1}{2}$ ], giving rise to chains along the [10 $\bar{1}$ ] direction. These chains are connected by two other intermolecular hydrogen bonds along the [010] direction involving the water molecule, *viz.* O2—H21...O4 and O4—H41...O3<sup>ii</sup> [symmetry code: (ii)  $-x + 1, -y + 1, -z + 1$ ], giving rise to an inversion-related dimer at  $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$  and generating an infinite two-dimensional network parallel to the (101) plane, as shown in Fig. 3. The relatively short *a* axis [ $a = 4.2920(1) \text{ \AA}$ ] leads to these two-dimensional networks being stacked along the *a* direction, in which they are linked by an O4—H42...O2 hydrogen bond to generate a strongly hydrogen-bonded three-dimensional network. This arrangement gives rise to no significant  $\pi$ – $\pi$  interactions; the shortest centroid–centroid separation is 5.53  $\text{\AA}$  between the centroid of the C1–C6 ring and that of the glide-related C8–C13 ring at  $(\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z)$ .

## Experimental

Commercial 3,4-dihydroxybenzophenone (Sigma–Aldrich) was used. Colourless prismatic crystals of (I) were obtained from a solution in a mixture of water, ethanol and methanol (1:1:1 *v/v/v*) by slow evaporation at room temperature.

### Crystal data

$C_{13}H_{10}O_3 \cdot H_2O$	$V = 1136.01(5) \text{ \AA}^3$
$M_r = 232.23$	$Z = 4$
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation
$a = 4.2920(1) \text{ \AA}$	$\mu = 0.10 \text{ mm}^{-1}$
$b = 23.2084(7) \text{ \AA}$	$T = 298 \text{ K}$
$c = 11.4552(3) \text{ \AA}$	$0.60 \times 0.15 \times 0.09 \text{ mm}$
$\beta = 95.393(2)^\circ$	

### Data collection

Nonius KappaCCD area-detector diffractometer	2444 independent reflections
4756 measured reflections	1692 reflections with $I > 2\sigma(I)$
	$R_{int} = 0.032$

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.050$	H atoms treated by a mixture of constrained and independent refinement
$wR(F^2) = 0.158$	$\Delta\rho_{max} = 0.20 \text{ e \AA}^{-3}$
$S = 1.07$	$\Delta\rho_{min} = -0.16 \text{ e \AA}^{-3}$
2444 reflections	
159 parameters	
2 restraints	

**Table 1**

Hydrogen-bond geometry ( $\text{\AA}, ^\circ$ ).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O2—H21...O4	0.82	1.81	2.6302 (15)	175
O3—H3...O1 <sup>i</sup>	0.82	1.87	2.6861 (14)	178
O4—H41...O3 <sup>ii</sup>	0.93	1.98	2.9043 (14)	170
O4—H42...O2 <sup>iii</sup>	0.92	2.00	2.8922 (16)	161

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

All H atoms were located in a difference Fourier synthesis. Those bound to C atoms and those of the 3- and 4-hydroxy groups were subsequently allowed for as riding on their parent atoms, with C—H = 0.93  $\text{\AA}$  and O—H = 0.82  $\text{\AA}$ , and with  $U_{iso}(H) = 1.2U_{eq}(C)$  for aromatic H atoms. The water H atoms were located by difference Fourier synthesis; their coordinates were initially restrained using a DFIX restraint of 0.97 (2)  $\text{\AA}$  and then fixed during the final refinement cycles. For all H atoms bonded to O atoms,  $U_{iso}(H)$  values were set at  $1.5U_{eq}(O)$ .

Data collection: *COLLECT* (Nonius, 2000); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* (Otwinowski & Minor, 1997) and *SCALEPACK*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *Mercury* (Macrae *et al.*, 2006); 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: FG3171). Services for accessing these data are described at the back of the journal.

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