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The Crystal and Molecular Structure of 2,4-Dihydroxybenzophenone (HHB)

BY BERNARD W. LIEBICH

Laboratoire de Cristallographie aux Rayons X, Université de Genève, 24 quai Ernest Ansermet,
CH-1211 Geneva 4, Switzerland

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Abstract

2,4-Dihydroxybenzophenone (HHB), $C_{13}H_{10}O_3$, is monoclinic, $P2_1/c$, $a = 7.272$ (4), $b = 19.121$ (15), $c = 7.595$ (6) Å, $\beta = 94.1$ (1)°, $U = 1053.4$ Å³, $Z = 4$, $M_r = 214.1$, $D_x = 1.35$ Mg m⁻³, $F(000) = 448$. The counter technique, direct methods and least-squares refinement were used to give $R = 5.4\%$ ($R_w = 3.8\%$) for 1064 reflexions measured at 293 K. An intramolecular hydrogen bond with $O(1)\cdots O(2) = 2.550$ (4) Å and an intermolecular hydrogen bond with $O(2)\cdots O(3) = 2.735$ (4) Å are present. The significant distortions observed in the ring formed by the intramolecular hydrogen bond as well as in the adjacent benzene ring are discussed.

Introduction

2,4-Dihydroxybenzophenone (HHB), also called Uvinul 400, is used in a similar way to several other *ortho*-substituted benzophenones as 'sunscreen agents' added to numerous synthetic materials such as plastics, fibres and even to such preparations as suntan lotions. These substances, which combine a high absorption in the UV range with an outstanding photostability, have been shown to prevent undesirable photochemical degradation.

Beckett & Porter (1963), studying the surprisingly low photochemical reactivity of HHB, showed that it depended on the presence on benzophenone of a hydroxy group in the *ortho* and/or *para* position. Previously Yang & Rivas (1961) had observed that photo-enolization takes place in 2-methylbenzophenone. The mechanism of this reaction was established later by flash photolysis on 2,4-dimethylbenzophenone (Porter & Tchir, 1970), showing the presence of several transients, the photo-enol reverting by dark reaction to the initial form.

As with 2-hydroxy-4-methoxybenzophenone (HMB) and 2-hydroxy-4-methoxy-4'-chlorobenzophenone (HMCB), HHB forms complexes with H_3BO_3 in concentrated H_2SO_4 but, due to weaker fluorescence, is less suitable as a reagent for the determination of traces of boron (Liebich, 1971). The structure of HHB was determined after those of HMB (Liebich & Parthé, 1974a) and HMCB (Liebich, 1976) to provide further data on the nature of the hydrogen bonds found in this family of compounds.

Experimental

Pale-yellow, plate-like crystals of HHB were grown from alcohol solutions (EGA-CHEMIE KG). Precession photographs of the crystal indicated the centro-

symmetric space group $P2_1/c$ (No. 14) (systematic absences: $h0l$ with $l \neq 2n$, and $0k0$ with $k \neq 2n$).

1230 intensities were collected at 293 K on a Philips PW 1100 automatic diffractometer (ω - 2θ scan, Mo $K\alpha$ radiation, $\lambda = 0.7107 \text{ \AA}$, graphite monochromator). The crystal data of HHB are given in Table 1.

The structure was solved by direct methods with the program *LSAM* (Main, Woolfson & Germain, 1972). The refinement was carried out with *CRYSLQ* (XRAY system, 1976).

The function minimized was $\sum w(\Delta F_o^2)$ with weights $w = 1/\sigma^2(F_o)$. The scattering factors for C and O were from Cromer & Mann (1968), and for H from Stewart, Davidson & Simpson (1965).*

* Lists of structure factors and positional and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34211 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, CH1 2HU, England.

Table 1. Crystal data of 2,4-dihydroxybenzophenone (HHB)

$C_{13}H_{10}O_3$	$Z = 4$
Space group $P2_1/c$	$M_r = 214.1$
$a = 7.272(4) \text{ \AA}$	$U (\text{\AA}^3) = 1053.4$
$b = 19.121(15)$	$D_x (\text{Mg m}^{-3}) = 1.35$
$c = 7.595(6)$	
$\beta = 94.1(1)^\circ$	

Table 2. Atomic positional parameters ($\times 10^4$ for C and O; $\times 10^3$ for H)

E.s.d.'s are given in parentheses, except for H(O1) and H(O3) which were kept fixed in the final refinement.

	x	y	z
C(1)	3350(4)	2760(2)	9156(5)
C(2)	3093(4)	2029(2)	9118(5)
C(3)	4484(4)	1578(2)	9738(5)
C(4)	6151(4)	1850(2)	10421(5)
C(5)	6454(4)	2567(2)	10423(5)
C(6)	5093(4)	3010(2)	9793(5)
C(7)	1884(5)	3224(2)	8475(5)
C(1')	2039(5)	3999(2)	8617(5)
C(2')	1517(5)	4391(2)	7135(5)
C(3')	1565(6)	5108(2)	7221(7)
C(4')	2078(6)	5442(2)	8770(8)
C(5')	2566(6)	5057(2)	10256(6)
C(6')	2573(5)	4330(2)	10185(5)
O(2)	439(3)	2979(1)	7714(3)
O(1)	1474(3)	1735(1)	8487(3)
O(3)	7428(3)	1382(1)	11057(3)
H(C3)	433(3)	105(1)	972(3)
H(C5)	762(3)	277(1)	1080(4)
H(C6)	528(3)	351(1)	974(3)
H(C2')	114(4)	415(1)	605(4)
H(C3')	122(4)	537(1)	626(4)
H(C4')	205(4)	597(2)	890(4)
H(C5')	282(4)	524(1)	1132(4)
H(C6')	288(4)	404(1)	1121(4)
H(O1)	70	220	800
H(O3)	860	160	1170

In the preliminary stage of refinement, the data set was limited to $\sin \theta/\lambda \leq 0.3 \text{ \AA}^{-1}$. Later, atomic positions (Table 2) and anisotropic thermal parameters of the heavy atoms were refined by full-matrix least-squares calculations with all the data. The positions and the isotropic thermal parameters were refined for all H atoms except those participating in intra- and intermolecular hydrogen bonds. The latter H atoms were located from maxima in the Fourier difference map, at first refined and then kept fixed during the last cycles of refinement. The final cycle gave $R = \sum |\Delta F|/\sum |F_o| = 0.054$, for 1064 reflexions with $F \geq 3\sigma(F)$ (including those calculating greater than the 'less-than' threshold).

Discussion

The interatomic distances and angles of HHB calculated with *BONDLA* (XRAY system, 1976) are given in Fig. 1. Tables 3, 4 and 5 provide selected angles ($^\circ$), distances (\AA), torsion angles ($^\circ$) and

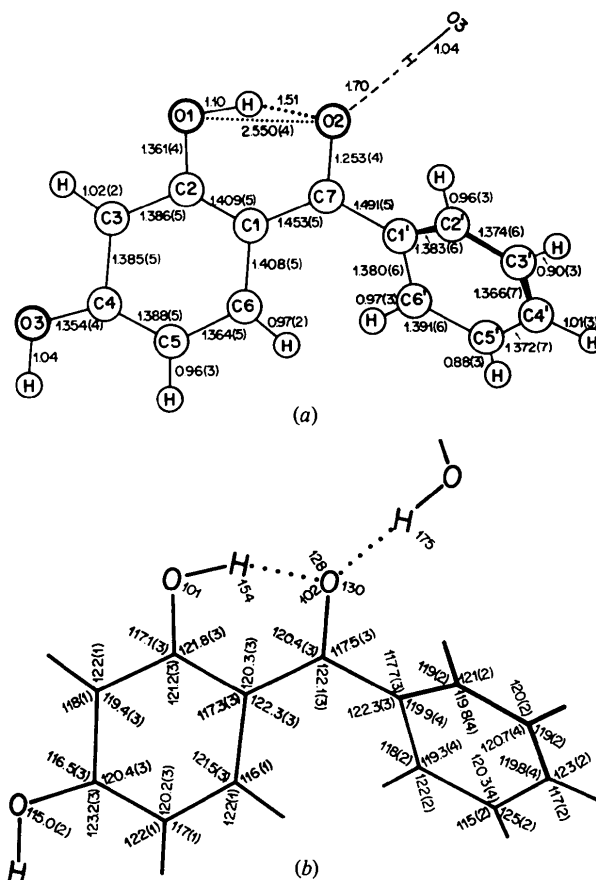


Fig. 1. Projection of the 2,4-dihydroxybenzophenone (HHB) molecule, showing the numbering scheme and interatomic distances (\AA) and angles ($^\circ$). E.s.d.'s are given in parentheses for the refined atomic positions.

Table 3. Angles ($^{\circ}$) and distances (\AA) around the intramolecular hydrogen bond of HHB

E.s.d.'s are given in parentheses except for quantities involving H. The corresponding averaged angles and distances of HMB and HMCB are given in square brackets.

C(2)—O(1)—H(O1)	101	[105]		
O(1)—H(O1)—O(2)	154	[152]		
C(7)—O(2)—H(O1)	102	[100]	O(2)—O(1)	2.550 (4) [2.546]
C(1)—C(7)—O(2)	120.4 (3)	[120.6]	O(1)—H(O1)	1.10 [0.92]
O(1)—C(2)—C(1)	121.8 (3)	[121.9]	H(O1)—O(2)	1.51 [1.67]
O(2)—C(7)—C(1')	117.5 (3)	[117.1]	O(1)—C(2)	1.361 (4) [1.355]
C(3)—C(2)—O(1)	117.1 (3)	[116.7]	O(2)—C(7)	1.253 (4) [1.251]
C(1)—C(7)—C(1')	122.1 (3)	[122.4]	C(1)—C(7)	1.453 (5) [1.461]
C(6)—C(1)—C(7)	122.3 (3)	[122.7]		
C(2)—C(1)—C(7)	120.3 (3)	[120.1]		

Table 4. Torsion angles of one of the molecules of HHB ($^{\circ}$)

E.s.d.'s are given in parentheses except for angles involving H. The corresponding averaged torsion angles of HMB and HMCB are given in square brackets.

C(6)—C(1)—C(2)—O(1)	-178.4 (3)	[-178.3]
C(6)—C(1)—C(7)—O(2)	+170.8 (3)	[+169.3]
C(6)—C(1)—C(7)—C(1')	-8.1 (6)	[-11.6]
C(1)—C(2)—O(1)—H(O1)	+4.9	[+4.9]
C(3)—C(4)—O(3)—H(O3)[C(8)]	-172.8	[-2.9]
C(1)—C(7)—C(1')—C(6')	-49.5 (5)	[-45.4]

Table 5. Least-squares planes through a set of atoms and distances (\AA) of atoms from these planes for one molecule of HHB

The values in parentheses show the positional e.s.d.'s of the atoms (\AA). The corresponding averaged deviations from the least-squares planes for HMB and HMCB are given in square brackets. Atoms with asterisks were included in the least-squares planes.

Plane 1		Plane 2	
C(1)*	+0.017 (4) [+0.014]	C(1)	+0.027 (4) [+0.024]
C(2)*	-0.005 (4) [-0.011]	C(2)*	+0.004 (4) [-0.003]
C(3)*	-0.012 (4) [-0.002]	C(3)*	-0.004 (4) [+0.003]
C(4)*	+0.016 (4) [+0.012]	C(4)	+0.022 (4) [+0.015]
C(5)*	-0.003 (4) [-0.008]	C(5)*	+0.004 (4) [-0.003]
C(6)*	-0.013 (4) [-0.005]	C(6)*	-0.004 (4) [+0.003]
C(7)	+0.003 (4) [+0.010]	C(7)	+0.015 (4) [+0.024]
O(1)	-0.011 (2) [-0.030]	O(3)	+0.057 (2) [+0.046]
O(2)	-0.142 (2) [-0.176]	Plane 3	
O(3)	+0.052 (2) [0.041]	O(1)*	+0.031 (2) [+0.036]
		O(2)*	-0.039 (2) [-0.048]
		C(2)*	-0.028 (4) [-0.029]
		C(1)*	-0.009 (4) [-0.016]
		C(7)*	+0.045 (4) [+0.057]

distances (\AA) of atoms from least-squares planes for HHB with the corresponding averaged values for HMB and HMCB given in square brackets. Table 6 gives in addition several short intermolecular distances found in the structure of HHB.

Table 6. Short interatomic distances (\AA)

E.s.d.'s are given in parentheses for the refined atomic positions.

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

O(1)—O(2) ⁱ	3.394 (5)	O(3)—O(2) ⁱⁱ	2.735 (4)*
O(1)—C(2') ^j	3.507 (5)	C(4)—O(2) ⁱⁱ	3.477 (6)
C(2)—O(2) ^j	3.455 (7)	H(C5)—O(2) ⁱⁱ	2.82 (3)
C(6')—O(1) ^j	3.371 (5)	H(O3)—H(C2') ⁱⁱ	2.42 (3)
C(4)—C(6) ^j	3.471 (6)	H(O3)—O(2) ⁱⁱ	1.69*
C(2)—C(7) ^j	3.517 (6)	H(C5)—H(O1) ⁱⁱ	2.70 (3)
C(3)—C(2') ^j	3.459 (6)	H(O3)—H(O1) ⁱⁱ	2.89
C(3)—C(7) ^j	3.541 (7)	H(O3)—C(7) ⁱⁱ	2.68
O(1)—H(C2') ^j	2.61 (3)		
H(C6')—H(O3) ^j	2.80 (4)		
H(C3)—H(C2') ^j	2.62 (4)		
H(C6')—O(1) ^j	2.55 (3)		

* Interatomic distances belonging to the intermolecular hydrogen bond.

The enol ring

In HHB (HMB, HMCB) the intramolecular hydrogen bond is mainly characterized by distance O(1)—O(2) and angle O(1)—H(O1)—O(2) with respectively values around 2.55 \AA and 154 $^{\circ}$. This intramolecular hydrogen bond might explain why distances C(2)—O(1) and C(7)—O(2) are shortened and lengthened respectively by about 0.05 \AA as compared with the normally expected values for C=O and C—OH, whereas distance C(1)—C(7) of ~ 1.45 \AA shows a negative deviation of about 0.05 \AA from a normal C—C single bond. Significant positive and negative deviations from 120 $^{\circ}$ for angles around C(1), C(2) and C(7) are noted. The enol ring in HHB is significantly distorted as shown by the deviations from plane 1 (Table 5) of atoms O(2) and O(1) [respectively -(+)0.140 and -(+)0.020 \AA], as well as by the deviations from least-squares plane 3 through atoms O(1), O(2), C(2), C(1), C(7) forming the enol ring. This feature is also suggested by the torsion angles C(6)—C(1)—C(2)—O(1) and C(6)—C(1)—C(7)—O(2) with values respectively of -(+)178.4 and +(-)170.8 $^{\circ}$ (Table 4).

The role of the H atom of the intramolecular hydrogen bond was of interest. The difference Fourier map during the final refinement of HMB and HMCB had shown electron density of irregular shape with, however, maxima located near O(1), the positions of which could be refined. In HHB, however, the electron density observed between O(1) and O(2) could be resolved into two slightly overlapping peaks with different densities. The first near O(1) had a height equivalent to about $\frac{3}{4}$ of an H atom in a different location in HHB and the second, near O(2), to about $\frac{1}{4}$. Owing to its greater density only the position of the peak near O(1) was used in the final refinements. [The coordinates of the observed position of the second peak

are H(O2) (0.056, 0.243, 0.770).] It was observed, however, that the location of the second peak did not seem unreasonable for a hydrogen-atom position. If the second peak has physical meaning it would indicate a disordered H atom occupying two distinct positions near O(1) and O(2) respectively, with the approximate occupation factors of $\frac{3}{4}$ and $\frac{1}{4}$.

The benzene ring

During the study of HMB and HMCB, the shortening in the benzene ring of distances C(3)–C(4) and C(5)–C(6) was noticed (Liebich & Parthé, 1974*b*; Liebich, 1976). The study of the molecular structure of HHB shows that the bond distance C(5)–C(6) is also clearly shortened, but C(3)–C(4) less so (with values of 1.364 and 1.385 Å, respectively). A similar bond shortening was observed before for the corresponding bond distances in salicylic acid (Cochran, 1953), in which this feature was also found by more recent X-ray (Sundaralingam & Jensen, 1965) and neutron (Bacon & Jude, 1973) studies. Cochran (1953) had suggested that the bond shortening in salicylic acid was probably due to the significant contribution of a quinonoid resonance structure to the overall state of resonance. It is therefore of interest to note that a comparable bond shortening can also be observed in other molecular structures, as for example in 2,4-dinitrophenol (Iwasaki & Kawano, 1977), in which an enol ring of different chemical nature is present in a similar location on the benzene ring.

In the benzene rings [C(1) to C(6)] of HMB and HMCB, the angles at C(2), C(4), C(6) were shown to be about 2° larger, and the angles at C(1), C(3), C(5) about 1–3° smaller, than 120° (Liebich, 1976). In the molecular structure of HHB the deviations of the angles at C(2), C(1), C(6) are very similar to those of HMB and HMCB, whereas the deviations of angles at C(3), C(4) and C(5) with –OH on C(4) are small. The relation between the angular deviations and substituent effects was studied for compounds with mono- and disubstituted benzene rings (Domenicano, Vaciago & Coulson, 1975; Domenicano, Mazzeo & Vaciago, 1976). These studies show that the angular deviations are significant and suggest that the angle (α) at the substituted carbon depends mainly on the σ -electron-withdrawing or releasing properties of the substituent as well as to some extent on conjugation. In HHB, HMB and HMCB the angles at C(1) with values around 117° are near to the lower limit for the mean values of α observed with first-row functional groups (Domenicano, Mazzeo & Vaciago, 1976). For the same compounds the observed angles β at C(2) and C(6), with values around 121.5°, show deviations in opposite directions with respect to that of the angle α at C(1). These deviations are usually associated with that of the angle α , and seem to be little influenced by the presence of the –OH group at C(2).

It appears that in HHB, HMCB, HMB, 2,4-dinitrophenol and salicylic acid, the benzene rings [C(1) to C(6)] show on the whole rather similar bond shortenings, especially pronounced for the distance C(5)–C(6). In opposition to this, the angular deviations in the same rings vary greatly according to the nature and position of the substituents. It appears from these examples that the angle and bond deviations of the benzene ring clearly bear valuable information on two superimposed effects, which may vary in different directions.

It is also of interest to note the slight deviations from planarity of the benzene ring [C(1) to C(6)] (Liebich, 1977) shown by several least-squares planes given in Table 5.

The intermolecular distances and molecular packing

Owing to the presence in HHB of an –OH group on C(4) which participates in the formation of an intermolecular hydrogen bond with O(2), each O(2) participates in both an intra- and an intermolecular hydrogen bond. This intermolecular hydrogen bond is characterized by the angle O(2)–H(O3)–O(3) of 175° and the distance O(2)···O(3) of 2.735 Å. Fig. 2 shows the packing of the molecules and how the intermolecular hydrogen bonds bind the molecules to form infinite chains.

As shown in Table 6 the intermolecular distances go down to 3.37 and 2.4 Å for, respectively, non-hydrogen and H···H contacts. Although the latter distances are rather short they remain in the range of the van der Waals radii. It can be noted with interest that several of the shorter distances are found between atoms belonging to the benzene–enol moieties of superimposed molecules (Fig. 3).

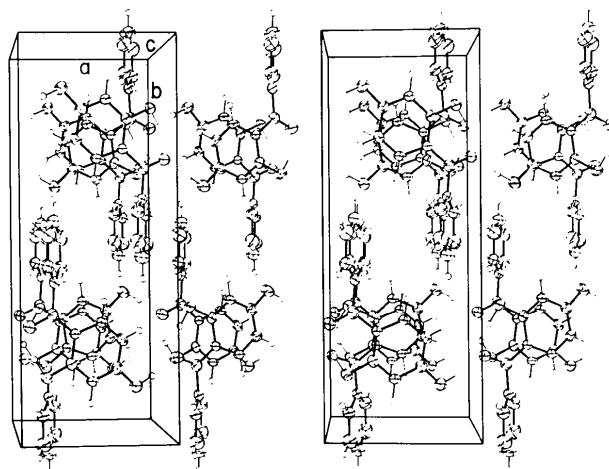


Fig. 2. Stereoscopic ORTEP drawing of HHB (XRAY system, 1976). Molecules outside the unit cell are included in order to show both the intra- and intermolecular hydrogen bonds and the molecular packing.

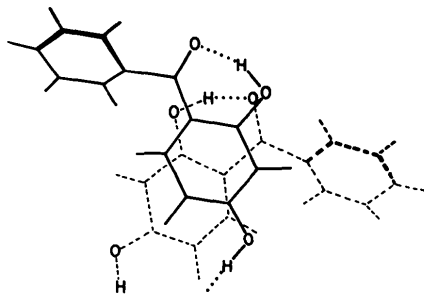


Fig. 3. Two superimposed molecules of HHB projected on the plane through the enol ring.

The packing of the molecules of HHB crystallizing in space group $P2_1/c$ is shown in Figs. 2 and 3. It can be noted that the benzene-enol moieties are approximately parallel. The stacking sequence is such that the molecules of HHB related by a centre of symmetry alternate. In addition the benzene rings [C(1') to C(6')] pointing out of these stacks are parallel to each other. It is also interesting to observe the presence of channels composed of superimposed intra- and intermolecular hydrogen bonds going through the crystal structure.

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