Table 2. *Distances* (Å) *and angles* (°) *involving hydrogen bonds, with e.s.d.'s in parentheses*

$O(2^*) = O(2)(1-x, 1-y, 1-z); O(3') = O(3)(x, y, 1+z)$.

O(1)···O(2*)	2·848 (4)	O(1)–H(O1)···O(3)	155·2 (2·7)
O(1)···O(3)	2·757 (4)	O(2*)–H(O2*)···O(1)	156·2 (2·7)
O(2*)···O(3′)	2·779 (5)	O(3′)–H(O3′)···O(2*)	160·8 (3·7)

molecules. By this, a two-dimensional network arises whose sheets are parallel to the (110) plane. The sheets can be regarded as consisting of zigzag chains running along [111] connected by the O(3)···O(1) and O(1)···O(2)($1-x$, $1-y$, $1-z$) hydrogen bonds; the chains are crosslinked by the hydrogen bond O(2)($1-x$, $1-y$, $1-z$)···O(3)($x, y, 1+z$). In DHMSB helices arise, also parallel to the **c** direction, but they connect the structure into a network in three dimensions. The bond data involving hydrogen bonds are in Table 2.

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2,2′-Dihydroxybenzophenone

BY E. O. SCHLEMPER

Department of Chemistry, University of Missouri, Columbia, Missouri 65211, *USA*

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Abstract. $C_{13}H_{10}O_3$, monoclinic, $P2_1/n$, $a = 7{\cdot}865\ (1)$, $b = 12{\cdot}237\ (2)$, $c = 11{\cdot}253\ (3)$ Å, $\beta = 109{\cdot}73\ (2)$°, $U = 1019{\cdot}5\ (6)$ Å^3, $Z = 4$, $M_r = 214{\cdot}1$, $D_x = 1{\cdot}396\ (3)$ g cm^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, $\mu = 1{\cdot}07$ cm^{-1}, $T = 295\ (1)$ K. The three-dimensional X-ray diffraction data were measured by the θ–2θ scan technique with a scintillation detector. The structure was solved by direct methods and refined by full-matrix least-squares techniques to $R(F_o) = 0{\cdot}033$ and $R_w(F_o) = 0{\cdot}046$ for 1278 reflections above 2σ. The two planar six-membered rings are separated by a dihedral angle of 45·7 (5)°. Bond distances and angles are normal. Effects of ring substituents on the bond distances involving the carbonyl C atom are discussed. Both hydroxyl groups act as intramolecular hydrogen-bond donors to the carbonyl O atom [O(2)···O(1), 2·656 (2); O(3)···O(1), 2·602 (2); H(O2)···O(1), 1·87 (3); H(O3)···O(1), 1·77 (2) Å; O(2)–H(O2)···O(1), 141·7 (5); and O(3)–H(O3)···O(1), 148·6 (5)°]. The O(3)–H(O3) group is also involved in a weak intramolecular hydrogen bond with another carbonyl O atom.

Introduction. Intramolecular hydrogen bonding in 2-hydroxybenzophenones has been confirmed by several X-ray studies: (1) 2-hydroxy-4-methoxybenzophenone (HMB) (Liebich & Parthé, 1974); (2) 4′-chloro-2-hydroxy-4-methoxybenzophenone (HMCB) (Liebich, 1976); (3) 2,4-dihydroxybenzophenone (HHB) (Liebich, 1979); and (4) 2,2′,4,4′-tetrahydroxybenzophenone (THB) (Schlemper, 1982). The study of THB was undertaken to examine the possibility of intramolecular hydrogen bonding of both the 2 and 2′ hydroxyl groups to the carbonyl O. This was found to be the case, but the hydrogen bonding was further complicated by the 4 and 4′ hydroxy groups which are involved in intermolecular hydrogen bonds. Several IR and ^{1}H and ^{13}C NMR studies (Merrill, 1961; Maciel & Savitsky, 1964; Sopchik & Kingsbury, 1979) have been reported for 2,2′-dihydroxybenzophenone which suggested both O—H groups have intramolecular hydrogen bonds with the carbonyl group, but the equality of the bonds is disputed. For these reasons the present study of 2,2′-dihydroxybenzophenone (DHP) was performed.

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Table 1. *Data-collection parameters*

Number of observations	2572
Number of unique observations	1794
Number of unique observations above 2σ	1278
Agreement factor for equivalent reflections	2·1%
Absorption correction	None
Scan method	θ–2θ step
Background	16 steps each side of peak
Peak	64 steps
Scan range in θ (°)	$0\cdot55 + 0\cdot35 \tan\theta$
Monochromator	Graphite
Scan speed	Variable to maintain 3% counting statistics on the net intensity to a maximum of 90 s/scan
$R[F_o > 2\sigma(F_o)]$	0·033
R (all reflections)	0·064
wR	0·046
Standard deviation of an observation of unit weight	1·34

Table 2. *Positional and isotropic thermal parameters, with e.s.d.'s in parentheses*

For nonhydrogen atoms $B_{eq} = \frac{4}{3}\sum_i\sum_j \beta_{ij}\,\mathbf{a}_i.\mathbf{a}_j$. Isotropic B values are given for the H atoms.

	x	y	z	B_{eq}/B (Å^2)
O(1)	0·3898 (2)	0·09712 (9)	−0·0819 (1)	4·80 (6)
O(2)	0·2681 (2)	0·09814 (9)	−0·3327 (1)	4·80 (5)
O(3)	0·4408 (2)	0·10033 (9)	0·1589 (1)	4·76 (5)
C(1)	0·3709 (2)	0·2572 (1)	−0·1991 (1)	3·05 (6)
C(2)	0·3205 (2)	0·2036 (1)	−0·3168 (1)	3·40 (7)
C(3)	0·3199 (2)	0·2603 (1)	−0·4229 (1)	4·20 (8)
C(4)	0·3793 (2)	0·3660 (2)	−0·4136 (2)	4·40 (8)
C(5)	0·4399 (2)	0·4182 (1)	−0·2980 (2)	4·00 (7)
C(6)	0·4340 (2)	0·3645 (1)	−0·1925 (1)	3·45 (6)
C(7)	0·3637 (2)	0·1974 (1)	−0·0872 (1)	3·35 (6)
C(8)	0·3245 (2)	0·2528 (1)	0·0166 (1)	3·16 (6)
C(9)	0·3657 (2)	0·2004 (1)	0·1348 (1)	3·54 (7)
C(10)	0·3308 (2)	0·2531 (1)	0·2329 (1)	4·24 (8)
C(11)	0·2491 (2)	0·3531 (2)	0·2150 (1)	4·27 (8)
C(12)	0·2018 (2)	0·4046 (1)	0·0985 (1)	4·02 (7)
C(13)	0·2393 (2)	0·3550 (1)	0·0013 (1)	3·50 (6)
H(O2)	0·295 (3)	0·066 (2)	−0·255 (2)	8·2 (5)
H(O3)	0·435 (3)	0·073 (2)	0·081 (2)	7·8 (5)
H(C3)	0·279 (2)	0·222 (1)	−0·501 (1)	5·8 (4)
H(C4)	0·383 (2)	0·404 (1)	−0·489 (1)	5·2 (4)
H(C5)	0·484 (2)	0·492 (1)	−0·291 (2)	5·0 (4)
H(C6)	0·475 (2)	0·400 (1)	−0·110 (1)	4·0 (3)
H(C10)	0·363 (2)	0·213 (1)	0·314 (2)	6·5 (4)
H(C11)	0·221 (2)	0·388 (1)	0·282 (2)	5·7 (4)
H(C12)	0·143 (2)	0·476 (1)	0·086 (1)	5·0 (4)
H(C13)	0·207 (2)	0·389 (1)	−0·079 (1)	4·6 (4)

A lemon-yellow crystal (~0·2 × 0·2 × 0·3 mm) of 2,2′-dihydroxybenzophenone was chosen from a sample from Aldrich Chemical Company and mounted in random orientation on an Enraf–Nonius CAD-4 automated diffractometer for data collection. The resulting unit-cell information and data-collection parameters are given in the *Abstract* and in Table 1.

The data were reduced in the normal manner without correction for absorption since several ψ scans indicated no significant variation. Three standard reflections were used to check crystal orientation after every 200 reflections, and the 25 reflections (2θ = 20–28°) used to determine the cell dimensions were recentered and used to generate a new orientation matrix when the three standard reflections were found to be significantly off center. In addition three standard reflections were measured after every 8000 s of X-ray exposure to check on crystal and instrument stability. These standards showed an almost linear decrease in intensity of about 10% during data collection (~48 h). The data were corrected for this effect. The systematic absence of 150 $h0l$ ($h + l$ odd) and $0k0$ (k odd) reflections measured during data collection confirms the choice of space group $P2_1/n$.

The structure was solved using *MULTAN* (Germain, Main & Woolfson, 1971) from the phase set of highest combined FOM. The C and O atoms were clearly resolved on the resulting E map. After full-matrix least-squares refinement [minimizing $\sum w(|F_o| - |F_c|)^2$] of these atoms, the H atoms were all located from a difference Fourier synthesis. Inclusion of these H atoms with isotropic temperature factors along with C and O atoms with anisotropic temperature factors and an isotropic extinction parameter (Zachariasen, 1967) (186 variables) gave a final $R = \sum ||F_o| - |F_c||/\sum F_o = 0\cdot033$ and $wR = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2} = 0\cdot046$ [$w = 1/\sigma^2(F_o)$, $\sigma^2(F_o^2) = \sigma^2_{\rm counting} + (0\cdot05F_o^2)^2$, and $\sigma^2(F_o) = \sigma^2(F_o^2)/4F_o^2$]. The resulting extinction parameter was $1\cdot95 \times 10^{-6}$. The maximum parameter shift on the last cycle was 0·15 times its e.s.d. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974).* The atomic positional parameters and B_{eq} values are included in Table 2.

Discussion. The interatomic distances for DHP are presented in Fig. 1, and the bond angles are in Table 3. The crystal structure consists of discrete molecules of DHP held together primarily by van der Waals attractions and by a weak intermolecular hydrogen bond [O(1)···O(3), 3·024 (2) Å]. Intermolecular distances, less than 3·5 Å, for the nonhydrogen atoms are given in Table 4.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36598 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

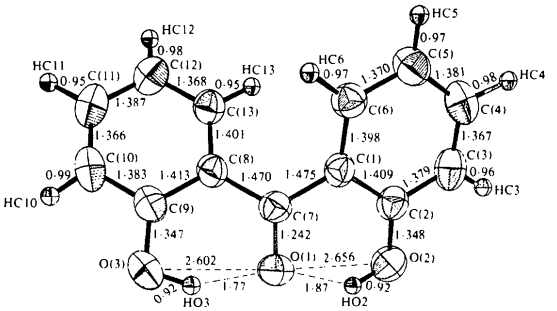

Fig. 1. Bond distances (Å), atom numbering and thermal ellipsoids (50% probability level) for 2,2′-dihydroxybenzophenone. Standard deviations in C—C, C—O, and O—O distances are 0·002 Å and those in C—H and O—H are 0·02 Å.

Table 3. *Selected bond angles* (°)

C(2)—C(1)—C(6)	118·0 (1)	C(1)—C(7)—C(8)	121·9 (1)
C(2)—C(1)—C(7)	119·5 (1)	C(7)—C(8)—C(9)	119·7 (1)
C(6)—C(1)—C(7)	122·4 (1)	C(7)—C(8)—C(13)	122·3 (1)
C(1)—C(2)—C(3)	119·8 (1)	C(9)—C(8)—C(13)	117·9 (1)
C(1)—C(2)—O(2)	123·1 (1)	C(8)—C(9)—C(10)	119·8 (1)
C(3)—C(2)—O(2)	117·1 (1)	C(8)—C(9)—O(3)	123·2 (1)
C(2)—C(3)—C(4)	120·6 (1)	C(10)—C(9)—O(3)	117·1 (1)
C(2)—C(3)—H(C3)	117 (1)	C(9)—C(10)—C(11)	120·7 (2)
C(4)—C(3)—H(C3)	123 (1)	C(9)—C(10)—H(C10)	116 (1)
C(3) C(4) C(5)	120·6 (2)	C(11)—C(10)—H(C10)	123 (1)
C(3)—C(4)—H(C4)	120 (1)	C(10)—C(11)—C(12)	120·6 (2)
C(5)—C(4)—H(C4)	120 (1)	C(10)—C(11)—H(C11)	120 (1)
C(4)—C(5)—C(6)	119·5 (2)	C(12)—C(11)—H(C11)	119 (1)
C(4)—C(5)—H(C5)	121 (1)	C(11)—C(12)—C(13)	119·5 (2)
C(6)—C(5)—H(C5)	120 (1)	C(11)—C(12)—H(C12)	120 (1)
C(1)—C(6)—C(5)	121·2 (1)	C(13)—C(12)—H(C12)	120 (1)
C(1)—C(6)—H(C6)	117·8 (8)	C(8)—C(13)—C(12)	121·5 (1)
C(5)—C(6)—H(C6)	120·9 (8)	C(8)—C(13)—H(C13)	118·1 (9)
O(1)—C(7)—C(1)	118·5 (1)	C(12)—C(13)—H(C13)	120·4 (9)
O(1)—C(7)—C(8)	119·6 (1)	O(2)—H(O2)···O(1)	141·7 (5)
		O(3)—H(O3)···O(1)	148·6 (5)

Table 4. *Intermolecular distances less than* 3·5 Å *involving non-hydrogen atoms*

O(1)···O(1)	3·146 (2) Å	O(2)···C(6)	3·328 (2) Å
O(1)···O(3)*	3·024 (2)	C(2)···C(11)	3·342 (2)
O(1)···C(5)	3·313 (2)	C(3)···C(7)	3·477 (2)
O(2)···O(3)	3·456 (2)	C(3)···C(11)	3·492 (2)
O(2)···C(5)	3·363 (2)		

* This is a very weak, intermolecular hydrogen bond [O(1)···H(O3), 2·50 (2) Å and O(1)···H(O3)—O3, 116 (1)°].

The thermal parameters ($B_{\rm eq}$, Table 2) indicate minimum thermal motion for the C atoms near the carbonyl bridge and increasing motion as one moves away from the bridge – a very reasonable result. The orientation of the ellipsoid axes (Fig. 1) suggests that there is considerable vibration of the entire molecular unit about an axis approximately perpendicular to the best plane through the entire molecule and through the center of mass.

Close contact [2·26 (4) Å] between the *ortho* H atoms [H(C6) and H(C13)] is probably largely responsible for the nonplanar nature of the molecule. The 45·7 (5)° dihedral angle between the aromatic rings is comparable to those (42 and 43°) in THP (Schlemper, 1982).

The chemically equivalent bond distances within the two six-membered rings are essentially identical and are in good agreement with the average values found for THP (Schlemper, 1982). The internal aromatic ring angles also show the same pattern as in THP, *i.e.* those involving the C atoms attached to the carbonyl O are significantly different from 120°. The α angles C(2)—C(1)—C(6) and C(9)—C(8)—C(13) are reduced to 118·0 (1) and 117·9 (1)° respectively while the internal β angles at C(6) and C(13) open to 121·2 (1) and 121·5 (1)° respectively. The major differences in molecular parameters from those in THP are the bond distances involving the carbonyl C atom. In THP the average C—C distance to the carbonyl C is 1·457 (4) Å while in DHP that distance is 1·472 (2) Å. In contrast, the C=O distance in DHP [1·242 (2) Å] is shorter than that in THP [1·264 (5) Å]. An intermediate value of 1·253 (4) Å was observed for the C=O distance in 2,4-dihydroxybenzophenone (HHB) (Liebich, 1979). In HHB the two C—C distances are 1·453 (5) and 1·491 (5) Å; the shorter one is to the 2,4-dihydroxy ring. This C—C distance is then apparently very sensitive to the substituents on the ring decreasing from 1·49 to 1·47 to 1·45 Å as the number of hydroxyl groups goes from 0 to 1 to 2 respectively. Both the variations in C—C distances and in C=O distance can be explained by electron donation from the hydroxyl groups through the aromatic system to the carbonyl group which strengthens the C—C bond, weakens the C=O bond, and increases the negative charge on the carbonyl O (see below).

The intramolecular hydrogen bonding in DHP (Fig. 1) is similar to that in the more symmetrical of the two independent molecules in THP in that both O···O distances are nearly identical [2·656 (2) and 2·602 (2) Å in DHP and 2·616 (2) and 2·584 (2) Å in THP]. However, those in DHP are significantly weaker (longer); this can be explained in terms of the greater electron-donating ability of the two hydroxyl groups in THP compared with only one in DHP as discussed above. The reason for the difference in the two intramolecular O···O hydrogen bonds in DHP is not evident. For the shorter one, O(1)···H—O(3), the hydroxyl group is also involved in a weak bifurcated intermolecular interaction [O(1)···O(3), 3·024 (2); O(1)···H(O3), 2·50 (2) Å; and O(1)···H(O3)—O(3), 116 (1)°]. The other hydroxyl group [O(2)—H(O2)] therefore appears to be somewhat deficient in hydrogen bonding. This nonequality of the hydrogen bonds may be the explanation of the unusual width of the ^{1}H NMR resonance reported by Merrill (1961). The weakening of the hydrogen-bond interaction relative to compounds such as 2,4-dihydroxybenzophenone [O···O, 2·550 (4) Å] which have only one intramolecular hydrogen bond to the carbonyl O is in keeping with the observed IR ν_{O-H} values (Merrill, 1961). Our findings are also consistent with the interpretation of the ^{13}C NMR and IR spectra by Sopchik & Kingsbury (1979) who suggested weaker hydrogen bonding than in single hydroxyl interactions with the carbonyl and also suggested unequal hydrogen bonding by the two hydroxyl groups.

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Structure of Tris(2-cyanoethyl)phosphine Oxide

By Bruce M. Foxman

Department of Chemistry, Brandeis University, Waltham, Massachusetts 02254, *USA*

Choong Hyun Kim

Department of Biophysics, Brandeis University, Waltham, Massachusetts 02254, *USA*

and Harry Mazurek

Department of Chemistry, Brandeis University, Waltham, Massachusetts 02254, *USA*

(*Received* 23 *September* 1980; *accepted* 6 *July* 1981)

Abstract. $C_9H_{12}N_3OP$, $M_r = 209{\cdot}2$, rhombohedral, $R3c$, $a = 13{\cdot}501$ (4), $c = 10{\cdot}177$ (3) Å, $Z = 6$, $D_m = 1{\cdot}30$ (1), $D_x = 1{\cdot}30$ Mg m^{-3}; $R = 0{\cdot}033$ for 615 reflexions. The molecule has threefold symmetry along the P—O bond with a C—P—C angle of 106·43 (12)°. The P=O distance is 1·485 (3) Å.

Introduction. Square-planar transition-metal complexes of the polyfunctional ligand, tris(2-cyanoethyl)phosphine, undergo a series of interesting solid-state reactions (Walton & Whyman, 1968; Foxman & Cheng, 1977). This ligand has both low steric requirements and the lowest basicity observed for a tertiary phosphine, $pK_a = 1{\cdot}37$ (Streuli, 1960). In order to examine the structural chemistry of related derivatives, the oxide was synthesized and its structure determined.

The space group, $R3c$, was implied from Weissenberg and precession photographs, and confirmed by the structure analysis and refinement. Density measurements were by flotation in xylene and carbon tetrachloride. Data were collected on a Syntex $P2_1$ diffractometer using a crystal with dimensions 0·11 × 0·13 × 0·39 mm, as described previously (Foxman, 1978). Details of the structure analysis are presented in Table 1. An empirical absorption correction (Syntex,

Table 1. *Data for the X-ray diffraction study of* $(O)P(CH_2CH_2CN)_3$

Cell-constant determination of 17 high-angle values in the range $82° < |2\theta| < 136°$ [λ(Cu $K\alpha_1$) = 1·5405 Å and Ni β-filter]; $T = 294$ K

Intensities measured: 655 total; 615 in unique set (to $2\theta = 158°$)

Data reduction as in Foxman (1978); e.s.d.'s of $|F_o|$ values calculated by method of finite differences (Churchill, Lashewycz & Rotella, 1977) gave $R_s = \sum\sigma(|F_o|)/\sum|F_o| = 0{\cdot}009$ [$I > 1{\cdot}96\sigma(I)$]

Full-matrix least-squares refinement: anisotropic thermal parameters for P, C, O, N atoms; isotropic thermal parameters for H atoms, with weights $= [\sigma^2(|F_o|) + (0{\cdot}035\,|F_o|)^2]^{-1}$

Final $R = \sum(||F_o| - |F_c||)/\sum|F_o| = 0{\cdot}033$,
$R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2} = 0{\cdot}042$

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