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Intramolecular Hydrogen Bonding in 2,2′,4,4′-Tetrahydroxybenzophenone

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Abstract

2,2′,4,4′-tetrahydroxybenzophenone, $C_{13}H_{10}O_5$, is triclinic, $P\bar{1}$, $a = 9{\cdot}950\,(2)$, $b = 12{\cdot}479\,(2)$, $c = 9{\cdot}334\,(1)$ Å, $\alpha = 98{\cdot}80\,(1)$, $\beta = 93{\cdot}22\,(1)$, $\gamma = 72{\cdot}45\,(1)°$, $U = 1091{\cdot}9$ Å^3, $Z = 4$, $M_r = 246{\cdot}1$, $D_x = 1{\cdot}498\,(1)$ Mg m^{-3}. 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 give $R(F_o) = 0{\cdot}034$ and $R_w(F_o) = 0{\cdot}047$ for the 2499 reflections above 2σ. There are two symmetry-independent molecules, each of which has two relatively strong intramolecular hydrogen bonds between *ortho* hydroxyl groups and the keto O atom. Because of differences in crystallographic environment (intermolecular hydrogen bonding), the O···O distances of the intramolecular hydrogen bonds are quite variable [2·516 (2) and 2·716 (2) Å in one molecule and 2·584 (2) and 2·616 (2) Å in the other molecule]. Each hydroxyl group is involved as either an intramolecular or intermolecular hydrogen-bond donor to another hydroxyl O atom or to a carbonyl O atom. The *ortho* hydroxyl group with the longest intramolecular O···O distance [2·716 (2) Å] is the donor for a bifurcated hydrogen bond. Systematic deviations from an ideal benzene-ring geometry are discussed.

Introduction

Several *ortho*-hydroxybenzophenone derivatives have absorption bands in the near ultraviolet. A number of these have found use as sun-protecting compounds in a variety of plastics and synthetic fabrics. Numerous patents exist for the use of these compounds on the international scene.

Liebich has reported X-ray diffraction structural determinations for three of these: (1) 2-hydroxy-4-methoxybenzophenone (HMB) (Liebich & Parthé, 1974); (2) 4′-chloro-2-hydroxy-4-methoxybenzophenone (HMCB) (Liebich, 1976); and (3) 2,4-dihydroxybenzophenone (HHB) (Liebich, 1979). All of these compounds have an intramolecular hydrogen bond of intermediate length (~2·55 Å).

2,2′,4,4′-Tetrahydroxybenzophenone (THB) is also widely used as an ultraviolet protecting agent (*e.g.*, Irie & Kametami, 1979) and has an intense yellow-orange color indicative of a shift to lower energy for its absorption band when compared with the other *ortho*-hydroxybenzophenones. The presence of *ortho*-hydroxy substituents on both rings provides the possibility for two intramolecular hydrogen bonds to the carbonyl oxygen. In order to examine that hypothesis, we have determined the structure of that compound.

Experimental

Yellow-orange prisms of THB (Aldrich Chemical Company) were grown from nitromethane solution by slow evaporation at room temperature. A crystal of approximate dimensions 0·2 × 0·3 × 0·4 mm was chosen for the X-ray study and mounted in random orientation on an Enraf–Nonius CAD-4 automated diffractometer for data collection. The crystals are triclinic ($P\bar{1}$) with crystal data shown in the *Abstract* based on a Delauney reduction of a cell obtained from automated centering of 25 reflections on the diffractometer. There are four molecules in the unit cell, therefore two independent molecules in the asymmetric unit of $P\bar{1}$ [$D_x = 1{\cdot}498\,(1)$ Mg m^{-3}].

Intensity data (294 K) were measured by the θ–2θ step-scan technique with Mo $K\alpha$ radiation ($\lambda = 0{\cdot}7107$ Å) from a graphite monochromator. A total of 3502 Bragg reflections were measured to a maximum 2θ of 47°. Three standard reflections measured after 8000 s of exposure showed no significant change with time. Several ψ scans indicated no significant absorption effects ($\mu = 0{\cdot}126$ mm^{-1}) so no absorption correction was applied. After averaging of equivalent reflections there were 3221 reflections of which the 2499 reflections with $F_o > 2\sigma(F_o)$ were used to solve and refine the structure [$\sigma^2(F_o^2) = \sigma^2$ counting $+ (0{\cdot}05 \times F_o^2)^2$ and $\sigma(F_o) = \sigma(F_o^2)/2F_o$].

The structure was solved by using *MULTAN* (Germain, Main & Woolfson, 1971) from the phase set of second highest combined FOM. The C and O atoms of the two symmetry-independent molecules were

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Table 1. *Positional and thermal parameters with e.s.d.'s*

	x	y	z	B_{eq} (Å^2)
O(1)	0·3327 (1)	0·0594 (1)	0·4953 (1)	4·17 (6)
O(2)	0·4613 (1)	−0·0774 (1)	0·2752 (1)	4·18 (6)
O(3)	0·2463 (2)	−0·0313 (1)	−0·1830 (1)	4·86 (7)
O(4)	0·2053 (1)	0·2165 (1)	0·7036 (1)	4·12 (6)
O(5)	−0·2852 (1)	0·2986 (1)	0·7236 (1)	4·22 (6)
O(1′)	0·4848 (1)	0·2687 (1)	0·5622 (1)	3·45 (6)
O(2′)	0·4976 (1)	0·1927 (1)	0·2961 (1)	4·21 (6)
O(3′)	0·1212 (2)	0·3593 (1)	−0·0068 (1)	4·60 (6)
O(4′)	0·4164 (1)	0·3268 (1)	0·8471 (1)	3·47 (6)
O(5′)	0·2459 (2)	0·7236 (1)	0·9856 (1)	4·87 (7)
C(1)	0·2257 (2)	0·0538 (1)	0·2647 (2)	2·73 (7)
C(2)	0·3468 (2)	−0·0246 (2)	0·1984 (2)	3·02 (7)
C(3)	0·3529 (2)	−0·0533 (2)	0·0503 (2)	3·52 (8)
C(4)	0·2422 (2)	−0·0035 (2)	−0·0362 (2)	3·42 (8)
C(5)	0·1236 (2)	0·0777 (2)	0·0247 (2)	3·26 (7)
C(6)	0·1168 (2)	0·1050 (2)	0·1718 (2)	2·97 (7)
C(7)	0·2201 (2)	0·0824 (1)	0·4221 (2)	2·91 (7)
C(8)	0·0871 (2)	0·1364 (1)	0·4993 (2)	2·67 (7)
C(9)	0·0851 (2)	0·2025 (2)	0·6366 (2)	2·93 (7)
C(10)	−0·0400 (2)	0·2576 (2)	0·7081 (2)	3·32 (7)
C(11)	−0·1639 (2)	0·2420 (2)	0·6491 (2)	2·99 (7)
C(12)	−0·1640 (2)	0·1690 (2)	0·5214 (2)	2·81 (7)
C(13)	−0·0399 (2)	0·1193 (1)	0·4474 (2)	2·70 (7)
C(1′)	0·3097 (2)	0·3532 (2)	0·4014 (2)	2·97 (8)
C(2′)	0·3739 (2)	0·2746 (2)	0·2811 (2)	2·99 (8)
C(3′)	0·3139 (2)	0·2781 (2)	0·1450 (2)	3·36 (8)
C(4′)	0·1854 (2)	0·3541 (2)	0·1255 (2)	3·47 (9)
C(5′)	0·1132 (2)	0·4272 (2)	0·2422 (2)	4·21 (9)
C(6′)	0·1754 (2)	0·4267 (2)	0·3772 (2)	4·10 (9)
C(7′)	0·3815 (2)	0·3540 (2)	0·5410 (2)	2·90 (7)
C(8′)	0·3433 (2)	0·4485 (2)	0·6584 (2)	2·92 (7)
C(9′)	0·3654 (2)	0·4314 (1)	0·8043 (2)	2·74 (7)
C(10′)	0·3312 (2)	0·5219 (2)	0·9152 (2)	3·12 (8)
C(11′)	0·2803 (2)	0·6312 (2)	0·8835 (2)	3·43 (8)
C(12′)	0·2626 (2)	0·6510 (2)	0·7406 (2)	4·06 (9)
C(13′)	0·2924 (2)	0·5617 (2)	0·6316 (2)	3·79 (8)
H(O2)	0·446 (2)	−0·038 (2)	0·369 (2)	6·3 (6)
H(O3)	0·334 (3)	−0·081 (2)	−0·201 (3)	8·3 (7)
H(O4)	0·282 (2)	0·159 (2)	0·649 (3)	7·2 (6)
H(O5)	−0·361 (3)	0·285 (2)	0·673 (3)	7·7 (7)
H(O2′)	0·511 (2)	0·199 (2)	0·401 (3)	6·5 (6)
H(O3′)	0·191 (4)	0·305 (3)	−0·089 (4)	13·5 (12)
H(O4′)	0·439 (2)	0·269 (2)	0·766 (2)	5·9 (6)
H(O5′)	0·272 (3)	0·703 (2)	1·078 (3)	7·3 (7)
H(C3)	0·433 (2)	−0·108 (2)	0·009 (2)	4·6 (5)
H(C5)	0·050 (2)	0·114 (1)	−0·035 (2)	3·7 (4)
H(C6)	0·038 (2)	0·164 (1)	0·211 (2)	2·8 (4)
H(C10)	−0·042 (2)	0·310 (2)	0·802 (2)	4·4 (5)
H(C12)	−0·249 (2)	0·154 (1)	0·487 (2)	3·3 (4)
H(C13)	−0·040 (2)	0·069 (1)	0·362 (2)	2·4 (3)
H(C3′)	0·363 (2)	0·223 (2)	0·062 (2)	4·7 (5)
H(C5′)	0·030 (2)	0·475 (2)	0·232 (2)	4·6 (5)
H(C6′)	0·125 (2)	0·478 (1)	0·458 (2)	3·4 (4)
H(C10′)	0·347 (2)	0·508 (1)	1·012 (2)	3·9 (4)
H(C12′)	0·229 (2)	0·724 (2)	0·722 (2)	4·5 (5)
H(C13′)	0·286 (2)	0·578 (2)	0·529 (2)	4·1 (4)

E.s.d.'s from the variance matrix of the full-matrix least-squares refinement are included in parentheses here and elsewhere in the manuscript. $B_{eq} = \frac{4}{3} \sum_i \sum_j \beta_{ij}\, \mathbf{a}_i . \mathbf{a}_j$.

clearly resolved. Full-matrix least-squares refinement of these atoms with anisotropic thermal parameters minimizing $\sum w(|F_o| - |F_c|)^2$ where $w = 1/[\sigma(F_o)]^2$ resulted in $R = \sum||F_o| - |F_c||/\sum F_o = 0{\cdot}071$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2} = 0{\cdot}110$. A difference Fourier map at this point revealed positions for all H atoms. Inclusion of these in the refinement with isotropic temperature factors gave $R = 0{\cdot}034$ and $R_w = 0{\cdot}047$. The refined isotropic extinction parameter (Zachariasen, 1967) was $1{\cdot}07 \times 10^{-6}$. The maximum parameter shift on the last cycle was 0·25 times its e.s.d., and the error in an observation of unit weight was 1·39. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974). The atomic positional parameters are included in Table 1.*

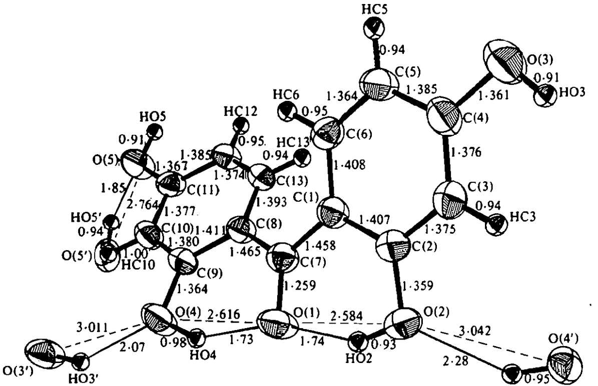

Fig. 1. Bond distances (Å), atom numbering, hydrogen bonding (Å) and thermal ellipsoids (50% probability level) for (unprimed) molecule 1 of THB. E.s.d.'s for O–O, C–O and C–C bonds are 0·002–0·003 Å and for O–H and C–H bonds 0·02–0·04 Å.

Discussion

The interatomic distances of THP and the hydrogen-bonding scheme are presented for the two independent molecules in Figs. 1 and 2. Bond angles are presented in Table 2. The packing of the two independent molecules (primed and unprimed) of the asymmetric unit in the unit cell is illustrated in Fig. 3. The primed molecules are those near the center of the cell. Besides the difference in intermolecular hydrogen bonding for the two independent molecules (see below), the crystal packing features nearly parallel packing of aromatic rings. Shorter intermolecular contacts and inter-

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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 36365 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

molecular hydrogen bonds are given in Table 3. The basic structural features of the two are very similar. The aromatic rings are each nearly planar with dihedral angles between the two six-membered rings within a molecule of 41·7 and 43·5° (Table 4). The major differences between the two molecules are found in (1) the pairs of intramolecular hydrogen bonds between the 2 and 2′ hydroxyl groups and the carbonyl oxygen (see below) and (2) the nature of the intermolecular hydrogen bonds (Figs. 1 and 2). In the primed molecule both the carbonyl oxygen and the oxygen of one of the *ortho* hydroxyl groups accept a hydrogen bond from a hydroxyl group of another molecule; in the unprimed molecule both *ortho* hydroxyl oxygens and one *para* hydroxyl oxygen accept hydrogen bonds from hydroxyls of other molecules. When compared with the intramolecular ones, these are relatively weak hydrogen bonds, and the O···O distances for these bonds range from 2·756 (2) to 3·042 (2) Å (Table 3). Each *para* hydroxyl group acts as an intermolecular hydrogen-bond donor to one other O atom, but, of the *para* hydroxyl groups, only O(5) is an acceptor of an intermolecular hydrogen bond. The *ortho* hydroxyl

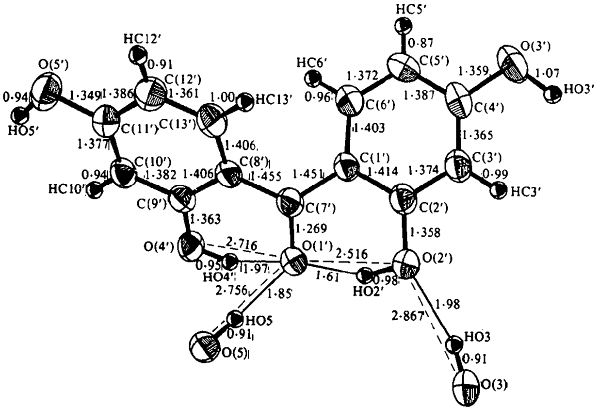


Fig. 2. Bond distances (Å), atom numbering, hydrogen bonding (Å) and thermal ellipsoids (50% probability level) for (primed) molecule 2 of THB. E.s.d.'s are as in Fig. 1.

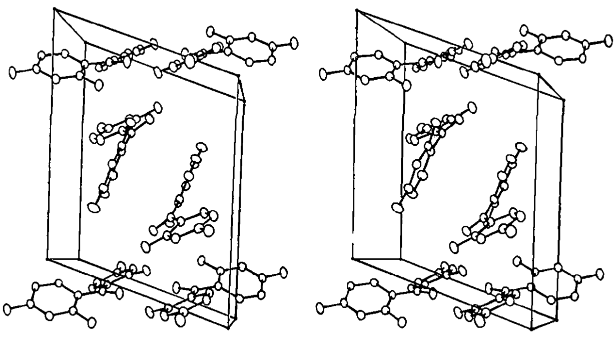


Fig. 3. Stereoscopic pair showing the packing of the molecules in the unit cell (H atoms omitted for clarity). The primed molecules are those near the center of the cell.

Table 2. *Bond angles* (°)

C(2)–C(1)–C(6)	116·7 (2)	C(9)–C(8)–C(13)	117·0 (2)
C(2)–C(1)–C(7)	120·0 (2)	C(9)–C(8)–C(7)	120·4 (2)
C(6)–C(1)–C(7)	123·2 (2)	C(7)–C(8)–C(13)	122·5 (2)
C(1)–C(2)–C(3)	120·7 (2)	C(8)–C(9)–C(10)	121·1 (2)
C(1)–C(2)–O(2)	122·8 (2)	C(8)–C(9)–O(4)	122·0 (2)
C(3)–C(2)–O(2)	116·6 (2)	C(10)–C(9)–O(4)	117·0 (2)
C(2)–C(3)–C(4)	120·6 (2)	C(9)–C(10)–C(11)	119·5 (2)
C(2)–C(3)–H(C3)	119 (1)	C(9)–C(10)–H(C10)	121 (1)
C(4)–C(3)–H(C3)	120 (1)	C(11)–C(10)–H(C10)	120 (1)
C(3)–C(4)–C(5)	120·4 (2)	C(10)–C(11)–C(12)	120·8 (2)
C(3)–C(4)–O(3)	121·3 (2)	C(10)–C(11)–O(5)	117·4 (2)
C(5)–C(4)–O(3)	118·2 (2)	C(12)–C(11)–O(5)	121·7 (2)
C(4)–C(5)–C(6)	119·0 (2)	C(11)–C(12)–C(13)	119·0 (2)
C(4)–C(5)–H(C5)	120 (1)	C(11)–C(12)–H(C12)	120 (1)
C(6)–C(5)–H(C5)	121 (1)	C(13)–C(12)–H(C12)	121 (1)
C(5)–C(6)–C(1)	122·6 (2)	C(12)–C(13)–C(8)	122·2 (2)
C(5)–C(6)–H(C6)	118 (1)	C(12)–C(13)–H(C13)	119 (1)
C(1)–C(6)–H(C6)	120 (1)	C(8)–C(13)–H(C13)	119 (1)
C(2)–O(2)–H(O2)	104 (2)	C(9)–O(4)–H(O4)	104 (1)
C(4)–O(3)–H(O3)	105 (2)	C(11)–O(5)–H(O5)	110 (2)
C(1)–C(7)–O(1)	119·4 (2)	C(8)–C(7)–O(1)	118·3 (2)
C(1)–C(7)–C(8)	122·3 (2)		
C(2′)–C(1′)–C(6′)	116·4 (2)	C(9′)–C(8′)–C(13′)	116·7 (2)
C(2′)–C(1′)–C(7′)	120·2 (2)	C(9′)–C(8′)–C(7′)	121·4 (2)
C(6′)–C(1′)–C(7′)	123·5 (2)	C(7′)–C(8′)–C(13′)	121·7 (2)
C(1′)–C(2′)–C(3′)	121·4 (2)	C(8′)–C(9′)–C(10′)	121·0 (2)
C(1′)–C(2′)–O(2′)	121·0 (2)	C(8′)–C(9′)–O(4′)	123·5 (2)
C(3′)–C(2′)–O(2′)	117·6 (2)	C(10′)–C(9′)–O(4′)	115·5 (2)
C(2′)–C(3′)–C(4′)	120·0 (2)	C(9′)–C(10′)–C(11′)	120·0 (2)
C(2′)–C(3′)–H(C3′)	120 (1)	C(9′)–C(10′)–H(C10′)	120 (1)
C(4′)–C(3′)–H(C3′)	120 (1)	C(11′)–C(10′)–H(C10′)	120 (1)
C(3′)–C(4′)–C(5′)	120·7 (2)	C(10′)–C(11′)–C(12′)	120·2 (2)
C(3′)–C(4′)–O(3′)	121·9 (2)	C(10′)–C(11′)–O(5′)	123·4 (2)
C(5′)–C(4′)–O(3′)	117·4 (2)	C(12′)–C(11′)–O(5′)	116·4 (2)
C(4′)–C(5′)–C(6′)	119·3 (2)	C(11′)–C(12′)–C(13′)	119·6 (2)
C(4′)–C(5′)–H(C5′)	122 (1)	C(11′)–C(12′)–H(C12′)	119 (1)
C(6′)–C(5′)–H(C5′)	119 (1)	C(13′)–C(12′)–H(C12′)	121 (1)
C(5′)–C(6′)–C(1′)	122·0 (2)	C(12′)–C(13′)–C(8′)	122·3 (2)
C(5′)–C(6′)–H(C6′)	119 (1)	C(12′)–C(13′)–H(C13′)	119 (1)
C(1′)–C(6′)–H(C6′)	119 (1)	C(8′)–C(13′)–H(C13′)	119 (1)
C(2′)–O(2′)–H(O2′)	103 (2)	C(9′)–O(4)–H(O4′)	111 (1)
C(4′)–O(3′)–H(O3′)	110 (2)	C(11′)–O(5′)–H(O5′)	111 (2)
C(1′)–C(7′)–O(1′)	118·7 (2)	C(8′)–C(7′)–O(1′)	117·7 (2)
C(1′)–C(7′)–C(8′)	123·6 (2)		

Table 3. *Shorter intermolecular contacts* (Å)

O(1)–O(2)	2·912 (2)	O(3)–C(13)	3·388 (2)
O(2)–O(1′)	2·921 (2)	O(4)–O(1′)	3·417 (2)
O(4)–O(4′)	2·994 (2)	O(5′)–C(4)	3·430 (2)
C(13)–C(13)	3·136 (3)	O(5)–C(9′)	3·441 (2)
O(5)–O(4′)	3·146 (2)	O(1)–O(2′)	3·442 (2)
O(3′)–O(4′)	3·196 (2)	O(2′)–C(2)	3·461 (2)
O(1)–O(1)	3·213 (2)	C(6)–C(4′)	3·469 (3)
O(4′)–C(3′)	3·217 (2)	C(7)–C(12)	3·469 (3)
O(5′)–C(3)	3·232 (2)	O(1′)–C(11)	3·470 (2)
O(2)–O(4)	3·258 (2)	O(2)–O(2′)	3·471 (2)
O(3′)–C(10)	3·314 (2)	C(8)–C(13)	3·473 (3)
O(3)–O(4)	3·322 (2)	C(12)–C(12′)	3·473 (3)
O(4)–C(7′)	3·351 (2)	C(1)–C(2′)	3·476 (3)
O(1)–O(1′)	3·360 (2)	O(4′)–C(4′)	3·476 (2)
O(1′)–C(12)	3·360 (2)	O(3′)–C(9′)	3·479 (2)
C(6′)–C(3′)	3·369 (3)	O(5′)–C(11)	3·483 (2)
		O(3′)–C(10′)	3·491 (2)

Intermolecular hydrogen bonds

	O···O	O–H	H···O	O–H···O
O(5)–H(O5)···O(1′)	2·756 (2)	0·91 (3)	1·85 (3)	175 (1)°
O(5′)–H(O5′)···O(5)	2·764 (2)	0·94 (3)	1·85 (3)	164 (1)
O(3)–H(O3)···O(2′)	2·867 (2)	0·91 (3)	1·98 (3)	164 (1)
O(3′)–H(O3′)···O(4)	3·011 (2)	1·07 (4)	2·07 (4)	146 (1)
O(4′)–H(O4′)···O(2)	3·042 (2)	0·95 (2)	2·28 (3)	137 (1)

Table 4. *Least-squares planes*

The first six atoms in each case were used to define the plane.

Plane 1		Plane 2		Plane 3		Plane 4		HHP	
C(1)	−0·018 (2)	C(8)	0·033 (2)	C(1′)	0·030 (2)	C(8′)	−0·014 (2)	C(1)	0·017 (4)
C(2)	0·016 (2)	C(9)	−0·037 (2)	C(2′)	−0·030 (2)	C(9′)	0·017 (2)	C(2)	−0·005 (4)
C(3)	0·000 (2)	C(10)	0·005 (2)	C(3′)	0·007 (2)	C(10′)	−0·009 (2)	C(3)	−0·012 (4)
C(4)	−0·014 (2)	C(11)	0·031 (2)	C(4′)	0·020 (2)	C(11′)	−0·007 (2)	C(4)	0·016 (4)
C(5)	0·010 (2)	C(12)	−0·029 (2)	C(5′)	−0·023 (2)	C(12′)	0·014 (2)	C(5)	−0·003 (4)
C(6)	0·007 (2)	C(13)	−0·002 (2)	C(6′)	−0·009 (2)	C(13′)	0·000 (2)	C(6)	−0·013 (4)
C(7)	−0·016 (2)	C(7)	0·043 (2)	C(7′)	0·109 (2)	C(7′)	0·039 (2)	C(7)	0·003 (4)
O(1)	0·338 (1)	O(1)	−0·491 (1)	O(1′)	−0·182 (1)	O(1′)	0·674 (1)	O(1)	−0·011 (2)
O(2)	0·039 (1)	O(4)	−0·130 (1)	O(2′)	−0·128 (1)	O(4′)	0·030 (1)	O(2)	−0·142 (2)
O(3)	−0·035 (2)	O(5)	0·077 (1)	O(3′)	0·037 (2)	O(5′)	−0·020 (1)	O(3)	0·052 (2)
H(O2)	0·22 (3)	H(O4)	−0·35 (2)	H(O2′)	−0·29 (2)	H(O4′)	0·07 (2)		
H(O3)	0·02 (3)	H(O5)	0·13 (3)	H(O3′)	0·16 (4)	H(O5′)	0·08 (3)		

Dihedral angles between planes (°)

Plane	Plane		Plane	Plane		Plane	Plane	
1	2	41·8 (5)	1	3	8·1 (3)	2	3	38·8 (5)
3	4	43·3 (5)	1	4	44·9 (5)	2	4	80·1 (5)

group O(4′)—H(O4′) is involved in a bifurcated donation to O(1′) (intramolecular) (Fig. 2) and O(2) (intermolecular) (Fig. 1). The O—H···O angles are all in the normal range [137 (2) to 175 (2)°]. The smallest angle [O(4′)—H(O4′)···O(2)] involves the bifurcated hydrogen bond; this O—H group is also involved in intramolecular hydrogen bonding to the carbonyl oxygen.

The benzene rings

In Fig. 4 the average values (with average deviation from the mean) of the chemically equivalent bond distances are presented. Liebich (1979) has noted the shortening of certain of the aromatic C—C distances, when compared with typical aromatic C—C distances of 1·39–1·40 Å, in a series of related complexes including HHB. As noted in that study the shortest distance is C(5)—C(6) [1·368 (5) Å in THB and 1·364 (5) Å in HHB]. The shortening of C(3)—C(4) suggested by some earlier studies (Liebich, 1979, and references therein) is not as pronounced here and is comparable with that for C(2)—C(3). In contrast there appears to be some lengthening of the distances involving C(1), particularly C(1)—C(2) [1·410 (3) Å] which is also long in HHB [1·409 (5) Å]. As in the other benzophenones the most significant deviation from 120° by a benzene ring angle is that of the *α* angle [C(2)—C(1)—C(6)], 116·7 (3)° in THB. While the *α* angle is contracted in THB, there is also a marked expansion in the adjacent *β* angle [C(1)—C(6)—C(5)] to 122·3 (2)°; this angle is also the largest angle in HHB. The other *β* angle [C(1)—C(2)—C(3)] is also significantly greater than 120° [121·1 (2)°]. One can conclude that the angles involving the carbon attached to the carbonyl group are all significantly different from 120° while the other three angles in the ring are very close to 120° (Table 2).

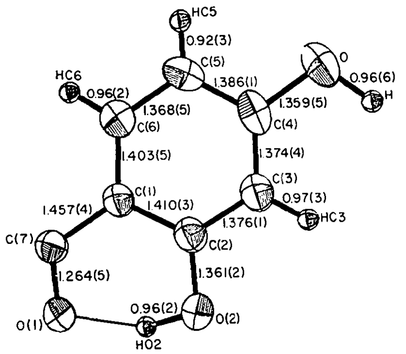
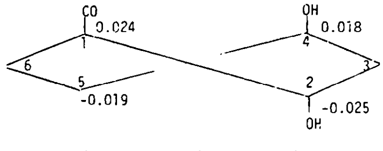


Fig. 4. Average values of chemically equivalent bond distances (Å).

A comparison of the deviations from planarity in the benzene rings (Table 4) reveals a consistent puckering of the planes, with the C(1) and C(4) carbons on one side of the least-squares plane and C(2) and C(5) on the other side. The average displacements (Å) of these carbons from the least-squares planes (perpendicular to sketch) are shown below.



A similar puckering was observed in HHB (Liebich, 1979).

Intramolecular hydrogen bonds

The main goal of this work was to examine the possibility of the presence of strong (short) intramolecular hydrogen bonds between the carbonyl oxygen and each of the *ortho* hydroxyl groups. In the previous studies of *ortho* hydroxybenzophenones (Liebich, 1976, 1979; Liebich & Parthé, 1974) the *ortho* hydroxyl was found to be strongly hydrogen bonded to the carbonyl oxygen (Table 5), but in no case were both aromatic rings substituted with *ortho* hydroxyl groups. This study reveals that indeed both *ortho* hydroxyl groups are intramolecularly hydrogen bonded to the carbonyl O atom in each of the symmetry-independent molecules (Figs. 1 and 2). The four independent O···O distances are, however, quite variable ranging from 2·516 (2) to 2·716 (2) Å.

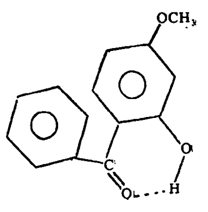
In the unprimed molecule, with O(2)···O(1) 2·584 (2) Å and O(4)···O(1) 2·616 (2) Å, the intramolecular interactions are nearly symmetric for the two *ortho* hydroxyl groups, whereas in the primed molecule O(2′)···O(1′) [2·516 (2) Å] is much shorter than O(4′)···O(1′) [2·716 (2) Å]. The O(4′) hydroxyl group is involved in a bifurcated hydrogen bond with an intermolecular O(4′)···O(2) distance of 3·042 (2) Å, H(O4′)···O(2) distance of 2·28 (2) Å, and O(4′)—H(O4′)···O(2) angle of 137 (2)°, whereas the other *ortho* hydroxyl H atoms are involved only in intramolecular interactions with carbonyl O atoms. In addition the carbonyl oxygen O(1′) acts as a hydrogen-bond acceptor for an intermolecular hydrogen bond from a *para* hydroxyl group [O(5)—H(O5)] (Fig. 2). In the unprimed molecule the intermolecular hydrogen bonds are nearly symmetrically arranged (Fig. 1). Thus the intramolecular hydrogen bonding in the primed molecule is much more perturbed by intermolecular hydrogen-bond effects, in keeping with the larger difference in intramolecular O···O distances.

In Table 5 the hydrogen bonds in this compound are compared with those observed in other enol ring systems. This comparison reveals two major points: (1) the hydrogen bond is shorter when the six-membered enol ring does not involve aromatic-ring C atoms as, for example, in benzoylacetone (Semmingsen, 1972) and (2) the hydrogen bond is lengthened and presumably weakened when the carbonyl oxygen accepts two intramolecular hydrogen bonds as in this study. In the previous studies by Liebich and co-workers on benzophenone compounds with only one *ortho* hydroxyl group the intramolecular O···O distance has been 2·55 Å in all cases. In THB the average intramolecular O···O distance is 2·608 Å. The increased length of the intramolecular hydrogen bonds in THB is consistent with an expected weakening of such hydrogen bonds when two hydroxyl groups share the same carbonyl-oxygen acceptor. However, an interesting effect can be

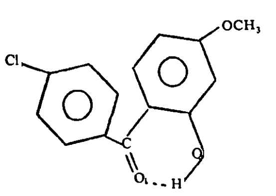
Table 5. *Comparison of intramolecular hydrogen bonds in some enol ring systems*

Compound		O···O	O—H	H···O	O—H···O	Reference
HMB		2·55 (1) Å	1·04 (5) Å	1·53 (5) Å	154 (2)°	Liebich & Parthé (1974)
HMCB		2·540 (7)	0·79 (5)	1·82 (5)	150 (2)	Liebich (1976)
HHB		2·550 (4)	1·10	1·51	154	Liebich (1979)
BA		2·498 (2)	1·18	1·40	154	Semmingsen (1972)
TEN		2·458 (3)	1·20 (4)	1·33 (4)	–	Kato (1971)
DBM		2·468	1·18	1·34	154	Williams (1966)
THB	unprimed molecule	2·584 (2)	0·93 (2)	1·74 (2)	149 (2)	This work
		2·616 (2)	0·98 (3)	1·73 (3)	148 (2)	This work
	primed molecule	2·516 (2)	0·98 (2)	1·61 (2)	152 (2)	This work
		2·716 (2)	0·95 (2)	1·97 (2)	133 (2)	This work

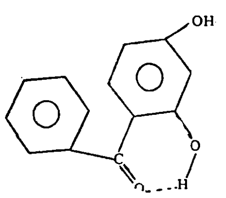
2-Hydroxy-4-methoxybenzophenone (HMB)



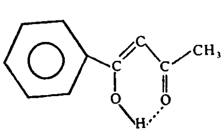
4′-Chloro-2-hydroxy-4-methoxybenzophenone (HMCB)



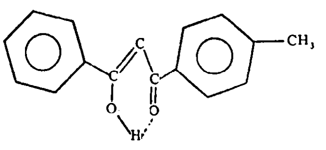
2,4-Dihydroxybenzophenone (HHB)



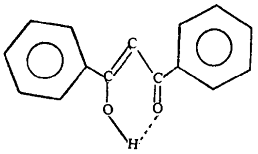
Benzoylacetone (BA)



p-Toluoylacetophenone (TEN)



Dibenzoylmethane (DBM)



seen in the more asymmetric molecule where one of the O···O distances is shorter than any of those observed in the molecules with a single *ortho* hydroxyl group. The reason for this apparent strengthening is not obvious.

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The Structures of 1,8-Dimorpholinonaphthalene and 1,8-Dipiperidinonaphthalene

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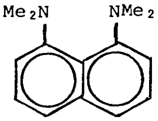
Abstract

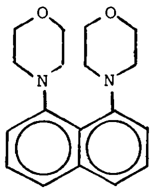
The structures of 1,8-dimorpholinonaphthalene (II) and 1,8-dipiperidinonaphthalene (III) have been determined. (II), $C_{18}H_{22}N_2O_2$, $M_r = 298{\cdot}4$, is monoclinic, $P2_1/c$, with $a = 11{\cdot}086\,(2)$, $b = 9{\cdot}870\,(1)$, $c = 16{\cdot}378\,(3)$ Å, $\beta = 121{\cdot}2\,(3)°$, $V = 1532{\cdot}9$ Å^3, $Z = 4$, $d_c = 1{\cdot}29$ g cm^{-3}, μ(Cu $K\alpha$) = $6{\cdot}68$ cm^{-1}. 1508 reflections were of significant intensity. The final R value is 0·059. (III), $C_{20}H_{26}N_2$, $M_r = 294{\cdot}2$, is triclinic, $P\bar{1}$, with $a = 9{\cdot}151\,(2)$, $b = 9{\cdot}380\,(2)$, $c = 10{\cdot}118\,(3)$ Å, $\alpha = 105{\cdot}9\,(5)$, $\beta = 98{\cdot}8\,(4)$, $\gamma = 94{\cdot}2\,(4)°$, $V = 819{\cdot}2$ Å^3, $Z = 2$, $d_c = 1{\cdot}19$ g cm^{-3}, μ(Cu $K\alpha$) = $5{\cdot}38$ cm^{-1}. 1956 reflections were of significant intensity. The final R value is 0·066. Both are strong bases in aqueous solution as is the bis(dimethylamino) analog (I). As expected, the naphthalene system is distorted in both (II) and (III) due to overcrowding. A survey of analyses of structures containing morpholine or piperidine rings shows both to be flexible. (II) shows the most pyramidal (least coplanar) bonds around nitrogen of any morpholine derivative previously studied. On the other hand, (III) is less pyramidal at nitrogen than are some other known structures containing the piperidine moiety. Possibly intermolecular forces acting on substituents in the 4-carbon position are responsible.

Introduction

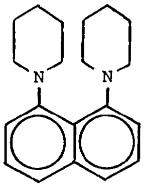
In our continuing study of the unusual acid–base properties of substances related to 1,8-bis(dimethylamino)naphthalene (I) (Alder, Bowman, Steele & Winterman, 1968; Hibbert, 1973, 1974; Einspahr, Robert, Marsh & Roberts, 1973) we have examined the proton-transfer reactions (Awwal, Burt & Kresge, 1981) and determined the crystal structures of 1,8-dimorpholinonaphthalene (II) and 1,8-dipiperidinonaphthalene (III). These studies form part of an attempt to relate the molecular structures of these materials to their acid–base behavior.



(I)



(II)



(III)

1,8-Dimorpholinonaphthalene (II)

Experimental

Needle-shaped crystals prepared by treating 1,8-diaminonaphthalene with 2,2′-dichlorodiethyl ether (Awwal, Burt & Kresge, 1981) were initially subjected to X-ray photographic examination. Cell parameters were determined from χ, φ and 2θ settings of 12 reflections on a Picker four-circle diffractometer using Ni-filtered Cu $K\alpha$ radiation.

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