is smaller than that of 164·6 (2)° found in 10-(3-methoxyphenyl)-5,10-dihydrophenarsazine. In other similar compounds, the values of the folding angles are: 154·1 (4)° in 10-methyl-5,10-dihydrophenarsazine (de Meester, Chu, Jovanovic & Biehl, 1986), 156·3° in 10-chlorophenoxarsine (Stuckey, Cordes, Handy, Perry & Fair, 1972), 169·2° in 10-chloro-5,10-dihydrophenarsazine (Camerman & Trotter, 1965), and 178·5° in 10,10′-thiodiphenoxarsine (Grindstaff, Cordes, Fair, Perry & Handy, 1972).

The *m*-tolyl substituent is in an axial position relative to the central ring as found in the compounds already mentioned. The phenyl ring is nearly perpendicular to the tricyclic ring. The angle between the phenyl plane and the benzo plane [C(1)C(2)C(3)C(4)C(4a)C(10a)] is −87·5 (2)° while with the benzo plane [C(5a)-C(6)C(7)C(8)C(9)C(9a)], it is 79·7 (2)°.* The orientation of the phenyl ring relative to the plane formed by the three atoms As(5), N(10) and C(1′) (bisecting the tricyclic ring) is given by the angle of 52·0 (1)° between these two planes, a value very similar to that of 50·7 (2)° found in 10-(3-methoxyphenyl)-5,10-dihydrophenarsazine.

The packing of the molecules in the unit cell is shown in the stereoscopic drawing of Fig. 2. There are no intermolecular distances less than the van der Waals separations. The shortest intermolecular contact is C(6)···N(10) of 3·435 (6) Å.

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* See previous footnote.

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Hydrogen Bonding in 2,3,4-Trihydroxyacetophenone

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Abstract. $C_8H_8O_4$, $M_r = 168·2$, monoclinic, $P2_1/c$, $a = 13·866$ (3), $b = 6·794$ (2), $c = 16·366$ (4) Å, $\beta = 101·27$ (3)°, $V = 1512$ (1) Å^3, $Z = 8$, $D_m = 1·46$, $D_x = 1·477$ (1) g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0·7107$ Å, $\mu = 1·12$ cm^{-1}, $F(000) = 704$, $T = 295$ (1) K, final $R = 0·044$ for 1131 observed reflections (θ–2θ scan) with $F_o^2 > 2\sigma(F_o^2)$. Extensive hydrogen bonding (inter- and intramolecular) is present involving all hydroxyl groups of the two independent molecules. Except for the 2-hydroxyl groups the hydrogen bonds are all bifurcated involving both inter- and intramolecular components. The 2-hydroxyl groups are strongly intramolecularly hydrogen bonded to the carbonyl oxygens [O(1)···O(2) = 2·512 (4), O(2)—H(O2) = 0·83 (4), O(1)···H(O2) = 1·76 (4) Å, O(2)—H(O2)···O(1) = 149 (3)°, O(1′)···O(2′) = 2·515 (4), O(2′)—H(O2′) = 0·88 (4), O(1′)···H(O2′) = 1·70 (4) Å, O(2′)—H(O2′)···O(1′) = 153 (3)°].

Introduction. In earlier X-ray diffraction studies of hydroxybenzophenone compounds strong intramolecular hydrogen bonding between *ortho* hydroxyl groups and the carbonyl oxygen was found. In 2,4-dihydroxybenzophenone (HHB) (Liebich, 1979) the O···O distance is 2·550 (4) Å; in 2,2′,4,4′-tetrahydroxybenzophenone (THB) (Schlemper, 1982*a*) it is 2·608 Å (av. of four); and in 2,2′-dihydroxybenzophenone (DHP) (Schlemper, 1982*b*) it is 2·629 Å (av. of two). In the latter two compounds each carbonyl oxygen accepts two intramolecular hydrogen bonds. No structural study of a comparable 2-hydroxyacetophenone has been done although recently (Chat-

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topadhyay, Banerjee, Mazumdar & Podder, 1985) the structure of 2,2-dichloro-2′-hydroxy-4′-methoxyacetophenone has been reported with an $O\cdots O$ distance of 2·589 (6) Å for the intramolecular hydrogen bond. Herein is reported, for comparison, the hydrogen bonding in 2,3,4-trihydroxyacetophenone.

Experimental. 2,3,4-Trihydroxyacetophenone from Aldrich Chemical Company was recrystallized from tetrahydrofuran by slow evaporation yielding needle-like crystals. Crystal approximately 0·10 × 0·15 × 0·45 mm chosen for data collection on Enraf–Nonius CAD-4 diffractometer with graphite-monochromated Mo $K\alpha$ radiation. 19 reflections ($2\theta = 12$–$37°$) used for cell parameters; no absorption correction (estimated range <2% based on ψ scans); 3194 reflections [range of hkl: hkl and $\bar{h}kl$ ($2\theta < 44°$) and $hk\bar{l}$ and $\bar{h}k\bar{l}$ ($2\theta < 34°$)]; three standard reflections after every 6000 s of X-ray exposure revealed no significant variation, three orientation check standards after every 150 reflections with recentering of all 19 reflections if any significant angular error; 1861 unique reflections (R_{int} on $F_o^2 = 0{\cdot}022$) [1131 with $F_o > 1{\cdot}5\sigma(F_o)$ used in refinement]; structure solved by *MULTAN* (Germain, Main & Woolfson, 1971); full-matrix least squares minimized $\sum w(|F_o| - |F_c|)^2$; H atoms from difference Fourier syntheses and chemical reasonableness [fixed with $B = 1$ Å^2 greater than the atom to which attached except hydroxyl hydrogens (x, y, z, B refined)]; 241 variables [x, y, z, 6β's nonhydrogen); $R = 0{\cdot}044$; $wR = 0{\cdot}052$; $S = 1{\cdot}35$; $w = 4F_o^2/(\sigma^2_{\text{counting}} + (0{\cdot}05F_o^2)^2]$; max. shift/e.s.d. = 0·05; no extinction correction; max. and min. $\Delta\rho$ on final difference map 0·4 and −0·4 e Å^{-3}; scattering factors including f' and f'' values from *International Tables for X-ray Crystallography* (1974); computations on PDP11/34 computer using Enraf–Nonius (1981) *SDP* programs.

Discussion. Final parameters for non-H atoms are in Table 1.* The molecular structures of the two independent molecules are essentially identical except for slight differences in hydrogen-atom positions (one of the molecules is shown in Fig. 1 with the atom numbering scheme). Table 2 gives the important bond distances and angles while Table 3 gives the hydrogen-bonding parameters. Except for hydrogen atoms the molecules are essentially planar. Methyl-hydrogen-atom positions on the primed and unprimed molecule are essentially mirror images while hydroxyl hydrogen positions are nearly the same in the two molecules. The dihedral angles between the aromatic ring and the three-atom plane of the acetyl group are 3·0 and 5·6° in the primed and unprimed molecule respectively. As observed by Liebich (1979, and references therein), there is clearly a shortening of the C(5)—C(6) and C(2)—C(3) distances [av. 1·373 (3) and 1·372 (3) Å] in the aromatic ring and, as noted in our earlier work (Schlemper, 1982*a*), a slight lengthening of the aromatic distances involving

Table 1. *Table of positional parameters and their e.s.d.'s*

	x	y	z	B_{eq}* (Å^2)
O(1)	0·0985 (2)	0·2072 (4)	0·2186 (2)	4·47 (7)
O(1′)	0·6064 (2)	0·2363 (4)	0·3094 (2)	4·47 (7)
O(2′)	0·5728 (2)	0·3855 (4)	0·4417 (1)	4·01 (6)
O(2)	0·0726 (2)	0·3797 (4)	0·0803 (1)	4·00 (6)
O(3′)	0·5755 (2)	0·3437 (4)	0·6081 (1)	4·44 (7)
O(3)	0·0816 (2)	0·3627 (4)	−0·0847 (2)	4·18 (6)
O(4′)	0·6271 (2)	−0·0026 (4)	0·6840 (2)	4·50 (7)
O(4)	0·1404 (2)	0·0292 (4)	−0·1500 (2)	4·59 (7)
C(1)	0·1252 (3)	0·0398 (6)	0·1004 (2)	3·04 (9)
C(1′)	0·6275 (3)	0·0510 (5)	0·4321 (2)	2·83 (8)
C(2′)	0·6003 (3)	0·2081 (5)	0·4778 (2)	2·77 (8)
C(2)	0·1008 (3)	0·2071 (5)	0·0501 (2)	2·90 (8)
C(3)	0·1046 (3)	0·2030 (5)	−0·0338 (2)	3·03 (9)
C(3′)	0·6005 (3)	0·1917 (6)	0·5619 (2)	3·11 (9)
C(4′)	0·6275 (3)	0·0180 (6)	0·6024 (2)	3·30 (9)
C(4)	0·1342 (3)	0·0344 (6)	−0·0683 (2)	3·29 (9)
C(5′)	0·6561 (3)	−0·1418 (6)	0·5593 (2)	3·8 (1)
C(5)	0·1589 (3)	−0·1322 (6)	−0·0202 (2)	3·58 (9)
C(6′)	0·6551 (3)	−0·1260 (6)	0·4757 (2)	3·61 (9)
C(6)	0·1535 (3)	−0·1299 (6)	0·0629 (2)	3·49 (9)
C(7′)	0·6273 (3)	0·0743 (6)	0·3435 (2)	3·37 (9)
C(7)	0·1182 (3)	0·0493 (6)	0·1875 (2)	3·46 (9)
C(8′)	0·6521 (4)	−0·0929 (7)	0·2930 (3)	5·5 (1)
C(8)	0·1339 (3)	−0·1310 (7)	0·2415 (3)	5·2 (1)

* $B_{\text{eq}} = \frac{4}{3}[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

Table 2. *Bond distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

O(1)	C(7)	1·240 (4)	C(1′)	C(6′)	1·412 (5)
O(1′)	C(7′)	1·242 (4)	C(1′)	C(7′)	1·459 (5)
O(2′)	C(2′)	1·364 (4)	C(2′)	C(3′)	1·380 (5)
O(2)	C(2)	1·360 (4)	C(2)	C(3)	1·385 (5)
O(3′)	C(3′)	1·365 (4)	C(3)	C(4)	1·375 (4)
O(3)	C(3)	1·367 (4)	C(3′)	C(4′)	1·370 (5)
O(4′)	C(4′)	1·344 (4)	C(4′)	C(5′)	1·393 (5)
O(4)	C(4)	1·356 (4)	C(4)	C(5)	1·384 (5)
C(1)	C(2)	1·405 (5)	C(5′)	C(6′)	1·371 (5)
C(1)	C(6)	1·398 (5)	C(5)	C(6)	1·376 (5)
C(1)	C(7)	1·450 (5)	C(7′)	C(8′)	1·483 (5)
C(1′)	C(2′)	1·397 (4)	C(7)	C(8)	1·500 (5)

C(2)	C(1)	C(6)	117·8 (3)	C(2′)	C(3′)	C(4′)	119·9 (3)
C(2)	C(1)	C(7)	119·1 (3)	O(4′)	C(4′)	C(3′)	121·1 (3)
C(6)	C(1)	C(7)	123·1 (4)	O(4′)	C(4′)	C(5′)	118·6 (3)
C(2′)	C(1′)	C(6′)	117·1 (3)	C(3′)	C(4′)	C(5′)	120·3 (3)
C(2′)	C(1′)	C(7′)	120·1 (3)	O(4)	C(4)	C(3)	120·5 (3)
C(6′)	C(1′)	C(7′)	122·8 (3)	O(4)	C(4)	C(5)	118·9 (3)
O(2′)	C(2′)	C(1′)	121·7 (3)	C(3)	C(4)	C(5)	120·5 (3)
O(2′)	C(2′)	C(3′)	116·7 (3)	C(4′)	C(5′)	C(6′)	119·7 (4)
C(1′)	C(2′)	C(3′)	121·6 (3)	C(4)	C(5)	C(6)	119·9 (4)
O(2)	C(2)	C(1)	122·6 (3)	C(1′)	C(6′)	C(5′)	121·3 (3)
O(2)	C(2)	C(3)	116·5 (3)	C(1)	C(6)	C(5)	121·1 (4)
C(1)	C(2)	C(3)	120·9 (3)	O(1′)	C(7′)	C(1′)	119·8 (3)
O(3)	C(3)	C(2)	122·6 (3)	O(1′)	C(7′)	C(8′)	119·2 (3)
O(3)	C(3)	C(4)	117·6 (3)	C(1′)	C(7′)	C(8′)	121·0 (4)
C(2)	C(3)	C(4)	119·8 (3)	O(1)	C(7)	C(1)	120·3 (3)
O(3′)	C(3′)	C(2′)	122·8 (3)	O(1)	C(7)	C(8)	118·9 (4)
O(3′)	C(3′)	C(4′)	117·3 (3)	C(1)	C(7)	C(8)	120·8 (4)

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* Lists of structure factors, H-atom parameters and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42760 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Hydrogen bonding in* 2,3,4-*trihydroxyacetophenone*

	O(1)···O(2) (Å)	O(1)–H (Å)	O(2)···H (Å)	O(1)–H···O(2) (°)	O(2) transformation*
O(2)–H(O2)···O(1)	2·512 (4)	0·83 (4)	1·76 (4)	149 (3)	(i)
O(2′)–H(O2′)···O(1′)	2·515 (4)	0·88 (4)	1·70 (4)	153 (3)	(i)
O(3)–H(O3)···O(2)	2·730 (4)	0·84 (4)	2·40 (4)	105 (3)	(i)
O(3)–H(O3)···O(2)	2·775 (4)	0·84 (4)	2·00 (4)	155 (3)	(ii)
O(3′)–H(O3′)···O(2′)	2·732 (4)	0·78 (4)	2·44 (4)	104 (3)	(i)
O(3′)–H(O3′)···O(2′)	2·761 (4)	0·78 (4)	2·03 (4)	157 (3)	(iii)
O(4)–H(O4)···O(3)	2·698 (4)	0·94 (4)	2·30 (4)	105 (3)	(i)
O(4)–H(O4)···O(1)	2·772 (4)	0·94 (4)	1·95 (4)	146 (3)	(iv)
O(4′)–H(O4′)···O(3′)	2·691 (4)	0·83 (4)	2·37 (4)	104 (3)	(i)
O(4′)–H(O4′)···O(1′)	2·793 (4)	0·83 (4)	2·01 (4)	158 (3)	(v)

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

C(1) [av. C(1)–C(6) = 1·405 (7) and C(1)–C(2) = 1·401 (4) Å]. The earlier work on benzophenones found the longer bond to be C(1)–C(2) (~ 1·41 Å). The present study is in reasonable agreement with the aromatic distances recently observed (Chattopadhyay *et al.*, 1985) for 2,2-dichloro-2′-hydroxy-4′-methoxyacetophenone where C(1)–C(6) = 1·405 (8), C(1)–C(2) = 1·401 (8), C(2)–C(3) = 1·388 (9) and C(5)–C(6) = 1·350 (8) Å despite the presence of the methoxy substituent.

However, the short intramolecular hydrogen bond between the 2-hydroxyl group and the carbonyl oxygen is significantly shorter in the present compound [O···O = 2·512 (4) and 2·515 (4) Å compared with 2·589 (6) Å in the methoxy derivative]. The title compound also has intramolecular hydrogen bonds, weaker than those above, between hydroxyl hydrogen atoms on O(3) and O(4) and the adjacent oxygens O(2) and O(3) respectively (Figs. 1 and 2 and Table 3). These same hydrogen atoms are involved in a bifurcated fashion with adjacent molecules [H(O3) and H(O3′) across layers to O(2) and O(2′) respectively and H(O4) and H(O4′) within the layers to O(1) and O(1′) respectively]. Thus, O(4) and O(4′) are not acceptors for any hydrogen bonds. The nearly parallel layers (roughly parallel to the *bc* face) are alternately linked by the across-layer hydrogen bonds while within layers the molecules are linked into chains along the **c** direction (Fig. 2). The intramolecular hydrogen bond in this study is shorter than any of those previously observed for the benzophenones (Schlemper, 1982*a*,*b*, and references therein) which range from 2·54 to 2·55 Å for a carbonyl oxygen accepting a single intramolecular hydrogen bond. Thus as might be expected replacement of a phenyl group with a methyl group increases the basicity, *i.e.* acceptor ability of the carbonyl oxygen. A similar but larger effect on this hydrogen bond is seen by replacement of the methyl group by a $CHCl_2$ group (Chattopadhyay *et al.*, 1985) where an even weaker hydrogen bond is found.

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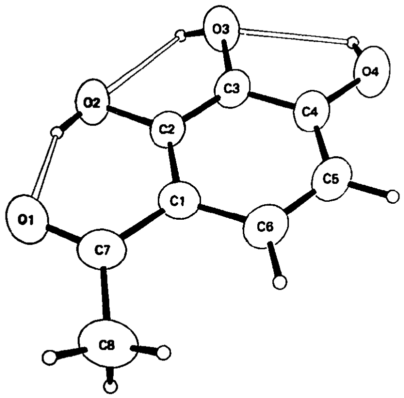

Fig. 1. Perspective view of one (unprimed) of the two independent molecules showing the atom labeling and thermal ellipsoids. The atoms in the other molecule (primed) are numbered in identical fashion.

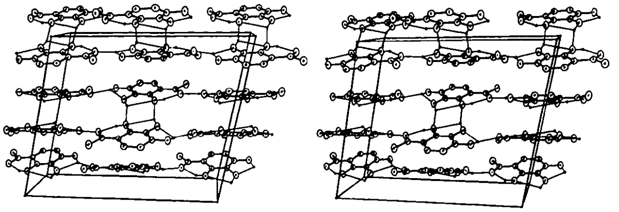

Fig. 2. Stereoscopic pair showing the extensive hydrogen bonds. Hydrogen bonds are the fine lines. The *c* axis is horizontal and the *a* axis is vertical.

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