The Crystal and Molecular Structure
of 4,4′-Dihydroxythiobenzophenone Monohydrate

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4,4′-Dihydroxythiobenzophenone monohydrate $(C_6H_4OH)_2CS.H_2O$, crystallizes in the monoclinic space group $P2_1/c$ (C_{2h}^5). There are four molecules in a unit cell of dimensions $a = 5.62$, $b = 10.95$, $c = 20.24$ Å, $\beta = 103.5°$. The crystal structure has been determined from two-dimensional X-ray data and the molecular geometry and dimensions have been established. Intermolecular hydrogen bonds are discussed.

Introduction

The colours of thiobenzophenone and most of its derivatives range from blue to green, but both 4-hydroxy- and 4,4′-dihydroxythiobenzophenone form red crystals. Brocklehurst (1956) has suggested that the red colour is probably due to the presence in the solid state of a comparatively strong hydrogen bond between a phenolic hydroxyl group and the sulphur atom of a neighbouring molecule, as indicated:
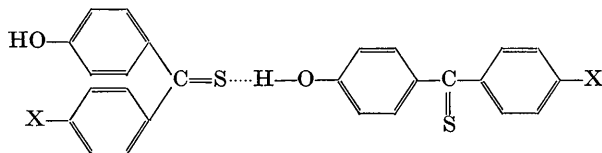
We considered that a crystal-structure analysis of one of these substances might resolve the question of the existence and possible structural significance of such a hydrogen bond. 4,4′-Dihydroxythiobenzophenone monohydrate was chosen for examination, and a few grams of the compound were kindly supplied by the late Dr A. Burawoy.

Experimental details and crystal data

Crystals suitable for X-ray examination were obtained by slowly cooling a warm saturated aqueous solution; these were red transparent needle-shaped prisms, elongated along the a axis. The crystal density was measured by flotation in a mixture of bromobenzene and xylene, and the unit-cell dimensions and the space group were determined from rotation and oscillation photographs taken about the a and b axes, and from $0kl$, $0k1$ and $h0l$ Weissenberg photographs.

The crystal data are summarized below:

Molecular formula: $(C_6H_4OH)_2CS.H_2O$.

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Molecular weight: 248·3. Melting point: 114 °C.
Unit cell: Monoclinic,

$$a = 5.62 \pm 0.01, \ b = 10.95 \pm 0.03, \ c = 20.24 \pm 0.06 \text{ Å},$$
$$\beta = 103° \ 30' \pm 15', \ V = 1211 \text{ Å}^3.$$

Four molecules per unit cell.
Number of electrons per unit cell, $F(000)$: 520.
Density, measured 1·36 g.cm^{-3},

$$\text{calculated } 1.36 \pm 0.01 \text{ g.cm}^{-3}.$$

Absent spectra: $h0l$ for $l = 2n + 1$, $0k0$ for $k = 2n + 1$.
Space group: $P2_1/c$ (C_{2h}^5).
Absorption coefficient for X-rays,

$$\lambda = 1.542 \text{ Å}; \ \mu = 23.7 \text{ cm}^{-1}.$$

The intensities of the $0kl$ and $h0l$ reflexions were recorded on multiple-film Weissenberg photographs, taken with copper $K\alpha$ radiation, the cross-sections of the crystals used for these two sets of photographs being 0·10 mm × 0·12 mm (a-axis specimen) and 0·06 mm × 0·18 mm (b-axis specimen). For each crystal, a calibration scale was prepared by recording a series of reflexions from a single set of planes, but with a range of exposure times, thus giving a set of spots of known relative intensities. The intensities of all reflexions were then estimated by visual comparison with these scales. In this way, 263 of the 281 accessible $0kl$ reflexions and 125 of the 147 accessible $h0l$ reflexions were measured.

Lorentz and polarization factors were introduced, and the relative structure amplitudes calculated. No absorption corrections were applied, as the specimens were considered to be sufficiently small for these to be neglected. The preliminary scale and overall temperature factors for the [100] projection were determined by Wilson's (1942) statistical method.

The [100] projection

Determination of the trial yz coordinates

An unsuccessful attempt was made to solve the structure by a direct method of approach, using the

procedure described by Woolfson (1957). An attempt to interpret the near-origin peaks of the sharpened Patterson function also failed; this is readily understood, as later analysis showed the benzene rings to be far from parallel to the plane of this projection. Approximate y and z coordinates were eventually obtained by the method of molecular location (Taylor & Morley, 1959) applied in conjunction with optical transform methods (Hanson, Lipson & Taylor, 1953), on the initial assumption that the atoms S, C(1), C(2), C(5), C(8), C(11), O(1), and O(2) (Fig. 1) were all coplanar.
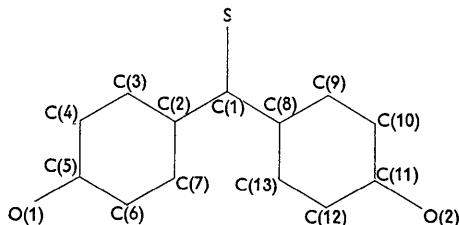

Fig. 1. The numbering of atoms in the molecule of 4,4'-dihydroxythiobenzophenone.

An examination of the $0kl$ section of the weighted reciprocal lattice indicated that the length of the molecule is roughly parallel to the $c \sin \beta$ direction, but it failed to reveal the orientation of the benzene rings as, owing to the symmetry operations, this projection has rings in four different orientations. The most promising inclination of the rings and of the molecule as a whole was obtained by comparing the weighted reciprocal lattice with the optical transforms of a few trial molecules. The molecular location method was then applied, and it proved capable of determining the position of the molecule although, as was shown by later refinement, neither the shape nor the orientation of the molecule was more than approximately correct. This will be described in a separate paper. At this stage, the agreement residual for all $0kl$ reflexions was 64%.

Refinement of the [100] *projection*

Atomic movements to fit a Fourier synthesis computed from the strong reflexions alone reduced the residual to 58%, after which a few cycles of least-squares refinement of the positional parameters, using reflexions up to $\sin \theta = 0.65$, brought the residual for these reflexions down to 40%. At this stage, the water molecule was included in a trial position and further refinement was attempted with Fourier and difference Fourier syntheses. Structure-factor graphs were also used but the structure would not refine beyond a residual of about 31%. It was not until a sharpened Patterson synthesis was examined by the superposition method that one benzene ring and its attached OH group was found to require considerable modification. After this change, three cycles of least-squares refinement followed by one

difference synthesis brought the residual down to 19% for reflexions up to $\sin \theta = 0.75$.

From this point, refinement was continued by successive $(F_o - F_c)$ syntheses based on the high angle reflexions ($\sin \theta > 0.45$), following Jellinek (1958a, b). When the appropriate peaks appeared on the low-angle difference map, the hydrogen atoms were introduced, assuming values of 1.08 and 0.96 Å for the C–H and O–H bond lengths. The values of the isotropic temperature factor, B, in the expression $\exp \{-B \sin^2 \theta / \lambda^2\}$ were 3.6, 4.0, 4.2, 4.7 and 5.2 respectively for the groups of atoms (C(1), C(2), C(8)), (C(3), C(11), C(13)), (C(6), C(7), C(12)), (O(2), C(4), C(5), C(9)) and (O(1), C(10) and hydrogen atoms). The isotropic temperature factors, B, for sulphur and for the oxygen atom of the water molecule were 3.8 and 5.5, but an allowance was made for a certain degree of anisotropy in the thermal vibrations of these atoms, using Curtis's program for structure-factor calculations (Curtis, 1959). The atomic scattering factors used were those of Viervoll & Øgrim (1949), Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955) and McWeeny (1951), in the analytic approximation of Forsyth & Wells (1959).

The final agreement residual, derived from the observed and calculated structure factors listed in Table 1, has a value of 9.6%. In this residual, an unobserved reflexion is included only if $|F_c|$ exceeds
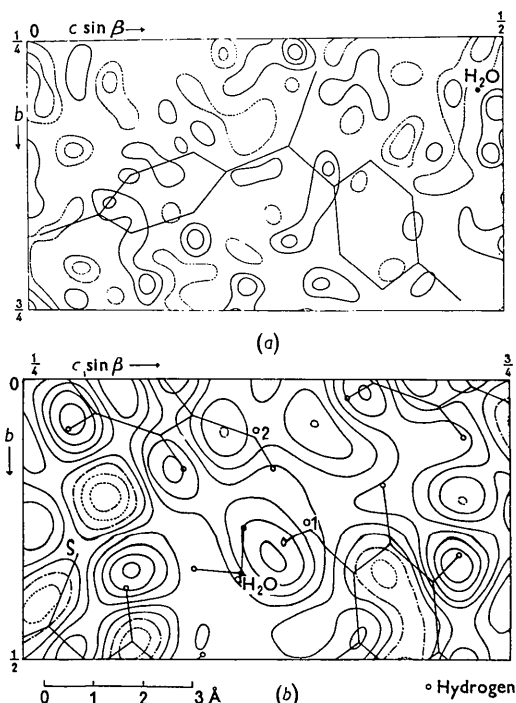

(a)

(b)

Fig. 2. (a) $(F_o - F_c)$ synthesis in the [100] projection. Contours are drawn at intervals of 0.2 e.Å^{-2}; the negative contours are broken and the zero contour is omitted. (b) $(F_o - F_c')$ synthesis illustrating the resolution of the hydrogen atoms. Contours are drawn at intervals of 0.1 e.Å^{-2}; the negative contours are dotted and the zero contour is broken.

Table 1. *Observed and calculated structure factors*

h	k	l	Fo	Fc	h	k	l	Fo	Fc	h	k	l	Fo	Fc	h	k	l	Fo	Fc	h	k	l	Fo	Fc	h	k	l	Fo	Fc	h	k	l	Fo	Fc
0	2	0	53.6	51.3	0	3	3	42.9	42.4	0	0	6	51.6	50.4	0	11	9	<5.4	3.7	0	11	11	8.4	7.6	0	2	15	<7.0	-2.8	0	9	18	<3.4	0.3
		4	24.1	21.9			4	<4.4	-0.4			1	41.1	43.2			12	<5.4	-2.0			12	<3.4	0.6			3	7.7	-6.6	0	1	19	8.4	-7.7
		6	20.2	21.0			5	22.1	-18.5			2	8.2	-12.0			13	3.4	3.5	0	0	12	<6.1	-6.1			4	8.7	7.0			2	10.0	-10.4
		8	15.7	-16.5			6	25.6	-24.5			3	<4.4	1.5	0	1	9	15.1	-15.2			1	25.6	24.9			5	10.4	9.4			3	<7.3	2.5
		10	8.6	6.9			7	<6.9	1.4			4	14.2	-11.6			2	6.1	4.4			2	27.3	24.9			6	<7.3	2.7			4	7.5	6.2
		-12	6.3	-3.6			8	8.7	9.1			5	14.1	-17.7			3	6.1	6.8			3	10.6	-12.6			7	10.0	-9.6			5	8.8	-8.7
		14	<3.4	-0.4			9	<7.0	-1.1			6	8.8	6.9			4	32.6	32.8			4	20.9	-20.7			8	<5.4	-0.3			6	<5.4	-1.1
0	1	1	<5.3	-4.4			10	<7.3	3.3			7	18.4	18.7			5	6.2	-4.3			5	23.5	-19.4			9	<5.4	-0.2			7	7.5	-5.1
		2	5.3	-2.3			11	<7.3	-5.5			8	8.8	6.9			6	9.6	-10.2			6	<7.0	-1.7			10	5.9	4.6			8	<3.4	2.2
		3	58.1	-55.3			12	<5.4	-1.0			9	19.7	-20.9			7	21.6	-23.4			7	8.6	-8.7	0	0	16	7.6	4.5			9	3.4	-4.8
		4	13.4	-11.4			13	7.3	8.3			10	<7.3	4.5			8	18.1	17.4			8	<7.3	-0.7			1	20.0	18.9	0	0	20	8.3	-5.7
		5	59.5	60.9	0	0	4	35.8	-35.9			11	<5.4	0.8			9	13.5	-19.9			9	10.6	-13.9			2	10.5	-10.3			1	<7.3	-0.9
		6	31.0	30.6			1	42.3	-40.8			12	<5.4	-4.3			10	<7.3	0.4			10	10.2	-9.5			3	<7.0	-0.6			2	9.8	-8.5
		7	3.7	2.5			2	41.4	-42.4			13	6.4	-4.7			11	6.9	-6.2			11	<3.4	4.1			4	<7.0	1.9			3	<5.4	3.3
		8	6.9	4.6			3	51.4	50.5	0	1	7	<4.5	0.7			12	6.6	-7.1	0	1	13	<6.9	-22.1			5	<7.3	3.1			4	<5.4	2.0
		9	7.0	-6.0			4	21.2	-22.7			2	26.7	26.3	0	0	10	59.5	57.4			3	21.8	24.9			6	<7.3	0.5			5	<5.4	-0.3
		10	7.5	-7.1			5	12.4	-12.9			3	31.0	32.5			1	9.9	6.8			4	12.9	-14.9			7	7.2	6.0			6	<5.4	4.3
		11	7.3	-5.9			6	10.6	-11.1			4	26.6	-27.7			2	15.9	11.7			5	16.5	-15.8			8	<5.4	-5.7			7	7.3	-6.7
		12	8.7	9.8			7	15.8	-16.3			5	<6.1	1.8			3	31.7	33.6			6	<7.0	-0.8			9	<5.4	2.2	0	1	21	8.0	8.4
		13	<3.4	-1.1			8	<6.9	1.2			6	11.6	11.6			4	8.8	-7.2			7	10.3	12.2			10	6.4	6.0			2	<5.4	1.1
		14	4.7	-6.3			9	17.3	17.2			7	9.6	8.4			5	8.8	-9.6			8	9.1	-9.4	0	1	17	9.5	-8.6			3	<5.4	1.3
0	0	2	14.3	-9.3			10	<7.3	2.4			8	<7.0	-0.9			6	16.5	17.0			9	<5.4	-2.2			2	7.6	5.9			4	6.1	-6.5
		1	<5.3	0.7			11	<7.3	-0.6			9	<7.0	3.2			7	<7.0	-0.1			10	<5.4	-2.5			3	8.6	5.7			5	6.0	5.8
		2	44.8	-46.7			12	<5.4	2.2			10	8.4	-6.9			8	9.6	-8.1			11	4.3	-3.0			4	11.8	-14.4	0	0	22	5.4	3.9
		3	37.4	38.0			13	<3.4	1.3			11	<5.4	-4.3			9	11.9	13.3	0	0	14	17.4	-20.0			5	<7.3	2.5			1	8.5	10.0
		4	33.0	-30.1	0	1	5	9.0	4.2			12	8.4	7.2			10	10.5	12.8			1	<6.9	-4.6			6	<7.3	4.6			2	<5.4	2.5
		5	4.4	-4.2			2	4.5	7.0			13	4.8	4.2			11	<5.4	0.3			2	<6.9	5.3			7	7.0	4.2			3	<5.4	-3.4
		6	22.9	-21.2			3	39.0	-37.5	0	0	8	39.0	-40.4			12	<3.4	0.4			3	6.9	5.3			8	<5.4	2.0			4	<3.4	3.4
		7	<6.1	-2.1			4	5.2	-5.3			1	11.6	-9.5	0	1	11	15.0	-16.4			4	<7.0	-3.0			9	<3.4	4.8	0	1	23	<3.4	1.3
		8	19.9	23.9			5	23.9	24.0			2	8.9	8.6			2	14.1	15.6			5	10.4	10.9	0	0	18	7.5	-6.8			2	<3.4	1.9
		9	22.5	-24.3			6	10.6	-11.4			3	15.9	14.9			3	16.7	-14.2			6	<7.3	-2.6			1	7.6	5.5			3	<3.4	2.6
		10	7.6	-5.8			7	8.8	-7.8			4	15.0	-15.5			4	14.0	-14.4			7	11.7	-14.7			2	11.8	13.4	0	0	24	<3.4	-0.3
		11	<7.3	-0.6			8	<6.9	3.2			5	12.3	-10.4			5	25.3	21.0			8	<7.3	-2.5			3	9.2	5.6			1	4.9	-5.5
		12	<5.4	2.4			9	<7.0	-1.1			6	10.6	-12.1			6	12.1	13.6			9	<5.4	1.4			4	<7.3	-0.5					
		13	<3.4	-1.1			10	<7.3	-0.9			7	8.0	6.5			7	19.1	18.6			10	<5.4	-0.8			5	<7.3	3.3					
		14	2.7	-1.2			11	9.0	10.4			8	17.4	18.2			8	8.6	9.4			11	3.5	-2.0			6	6.4	-6.3					
0	1	3	20.5	-21.5			12	<5.4	-1.8			9	8.6	9.3			9	<7.3	0.4	0	1	15	<6.9	-3.4			7	<5.4	-1.3					
		2	77.8	-75.8			13	4.3	-2.9			10	<7.3	1.4			10	6.3	-5.7								8	9.0	7.3					

h	k	l	Fo	Fc	h	k	l	Fo	Fc	h	k	l	Fo	Fc	h	k	l	Fo	Fc	h	k	l	Fo	Fc	h	k	l	Fo	Fc	h	k	l	Fo	Fc
1	0	0	40.8	-45.4	-1	0	10	14.0	13.8	2	0	16	<5.8	-7.2	3	0	2	34.6	30.6	3	0	16	29.0	26.2	4	0	10	17.8	-14.6	5	0	10	5.8	7.8
		2	13.2	-8.2			12	13.4	-12.4			18	<5.4	1.6			4	20.6	20.0			18	16.2	16.4			12	18.4	15.6			12	10.2	-13.2
		4	163.0	163.6			14	16.6	-17.4			20	6.6	8.2			6	19.4	-16.4			20	8.0	-7.8			14	23.6	23.4			14	6.8	-2.8
		6	23.2	22.2			16	<7.0	2.2	-2	0	2	39.6	35.0			8	<7.2	-7.8			22	6.2	3.8			16	10.4	-9.4			16	<5.4	-6.2
		8	25.4	-20.8			18	<7.0	-2.2			4	41.2	-39.8			10	10.0	-11.4	4	0	0	<7.2	-0.2			18	<5.4	0.6			18	<5.8	-1.0
		10	24.2	25.8			20	5.8	-2.0			6	40.8	53.2			12	<5.8	1.4			2	<7.2	-0.8			20	10.4	-9.4	6	0	0	11.2	-12.2
		12	8.8	-11.4			22	11.0	-9.2			8	<5.2	-3.2			14	<5.8	3.2			4	15.6	16.6	5	0	0	9.2	-7.2			2	<5.8	1.4
		14	12.4	10.0			24	7.6	-5.8			10	5.2	-0.8			16	13.0	-17.6			6	7.6	-7.2			2	19.0	22.4			4	<5.8	-4.8
		16	8.2	10.4	2	0	0	19.4	21.2			12	16.0	-10.4			18	<5.8	1.0			8	9.8	12.8			4	<5.4	-7.2	-5	0	2	<5.8	3.0
		18	9.2	-10.6			2	19.8	-19.6			14	28.6	-29.0	-3	0	2	19.2	17.8			10	<5.8	2.4			6	<5.4	-7.8			4	<5.8	5.0
		20	5.4	6.8			4	66.0	-65.4			16	18.8	16.0			4	<5.2	3.0			12	<5.4	-2.2			8	<5.4	2.8			6	<5.8	-1.6
		22	6.8	-5.6			6	35.6	-37.4			18	18.4	-19.4			6	45.8	44.4			14	8.6	7.2			10	8.2	-8.8			8	<5.8	1.2
-1	0	2	36.8	-36.8			8	22.2	19.8			20	5.8	-6.0			8	<5.8	2.0	-4	0	2	24.2	24.6	5	0	2	12.6	-11.6					
		4	29.2	-22.2			10	<5.2	3.0			22	12.2	12.2			10	<5.8	-1.6			4	<7.2	3.6			4	12.2	9.2					
		6	39.0	34.0			12	16.2	-16.2			24	7.6	-6.2			12	20.4	17.0			6	<7.2	1.4			6	9.0	-6.0					
		8	24.4	-21.6			14	7.0	-8.4	3	0	0	14.6	19.2			14	29.0	-29.2			8	24.8	20.2			8	13.8	11.6					

$F_{o\,min}$, the minimum observed structure factor in the appropriate range of $\sin\theta$; in this case, a term $(|F_c| - |F_{o\,min}|)$ is added to the numerator only. The final $(F_o - F_c)$ synthesis is shown in Fig. 2(a). The resolution of the hydrogen atoms is illustrated in Fig. 2(b), which is a low-angle difference synthesis computed with coefficients $(F_o - F'_c)$, where the F'_c's are structure factors calculated with the hydrogen atoms omitted. Fig. 3 gives the final F_o synthesis

Fig. 3. The projection of the electron density along the a axis. Contours are drawn at intervals of 1 e.Å^{-2} except at the sulphur atom, where the interval is 2 e.Å^{-2}. The broken line is at a level of 1 e.Å^{-2}.

computed from measured structure amplitudes and calculated signs.

The [010] projection

Determination of the trial x coordinates

From the assumed dimensions of the molecule and the known y and z coordinates, four possible projections of the molecule in the [010] direction were established; these involved alternative orientations of the benzene rings and of the molecule as a whole. The shape of the Patterson function and the fact that the 104 reflexion was very strong enabled one of these trial projections to be singled out as being correct. The remaining problem of locating the molecule in the unit cell was solved by considering the structure-factor graphs of the 100, 101 and 102 reflexions, and assuming hydrogen bonds O · · · H–O between phenolic OH groups of lengths known roughly from the literature. At this stage the agreement residual for all reflexions was 54%.

Refinement of the [010] projection

Three cycles of least-squares refinement of the x coordinates and of the scaling factor brought the residual down to 31%. A further slight improvement

was obtained by adjusting some atomic positions to correct a large discrepancy between F_o and F_c for the 200 reflexion. From this point onwards, the z coordinates were included in the refinement, which was carried out entirely by Fourier and difference Fourier syntheses. The positions of the hydrogen atoms of the benzene rings were postulated when the residual stood at 19%, and these, together with an anisotropic temperature factor for the sulphur atom, were then included in the structure factor calculations; the remaining hydrogen atoms, those taking part in the hydrogen bonds, were introduced later. The isotropic temperature factors, B, were respectively 4·3, 4·3, 4·8, and 6·3 for the sulphur atom and the groups of atoms (C(1), C(2), C(3), C(4), C(5), C(7)), (C(6), C(8), C(9), C(10), C(11), C(12), C(13), O(2)) and (O(1), O(H₂O) and hydrogen atoms).

The final agreement residual, based on the calculated and observed structure factors shown in Table 1, and computed as described above, is 10·7%. The final F_o synthesis is shown in Fig. 4.
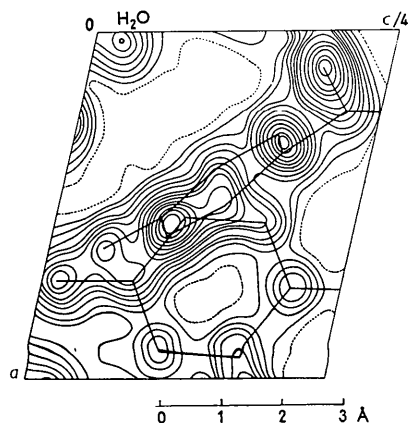
Fig. 4. The projection of the electron density along the b axis. The contour interval is 1 e.Å⁻² except at the sulphur atom, where it is 2 e.Å⁻² from 8 e.Å⁻² upwards. The broken line is at a level of 2 e.Å⁻².

The least-squares refinement of this structure and the Fourier syntheses were carried out on the Manchester University Mercury computer, using programs written by one of the authors (I. G. E.).

Description of the molecule

The final fractional coordinates of the atoms in the asymmetric unit are listed in Table 2; the z coordinates are the weighted means of the two sets of values deduced from the [100] and [010] projections. Standard deviations of the atomic coordinates have been obtained by Cruickshank's method (1949), taking $||sF_o| - |F_c||$ as a safe overestimate of $\sigma(F)$. The values of $\sigma(y)$ and $\sigma(z)$ have been determined for three resolved atoms: carbon, oxygen and sulphur; the value of $\sigma(x)$ has been estimated for a carbon atom

Table 2. *Final fractional atomic coordinates*

Atom	x	y	z
S	0·1098	−0·1913	0·1941
O(1)	0·6395	0·2330	0·0443
O(2)	0·2640	0·1088	0·4874
O(H₂O)	−0·0352	0·3459	0·4746
C(1)	0·2408	−0·0610	0·2226
C(2)	0·3596	0·0166	0·1765
C(3)	0·5160	−0·0352	0·1393
C(4)	0·6110	0·0341	0·0954
C(5)	0·5489	0·1596	0·0881
C(6)	0·4050	0·2117	0·1257
C(7)	0·3060	0·1441	0·1700
C(8)	0·2446	−0·0123	0·2908
C(9)	0·0576	−0·0498	0·3234
C(10)	0·0693	−0·0078	0·3906
C(11)	0·2648	0·0678	0·4233
C(12)	0·4500	0·1039	0·3907
C(13)	0·4325	0·0640	0·3240
H(C₃)	0·5614	−0·1311	0·1443
H(C₄)	0·7295	−0·0101	0·0663
H(C₆)	0·3621	0·3082	0·1199
H(C₇)	0·1851	0·1872	0·1987
H(C₉)	−0·0916	−0·1091	0·2978
H(C₁₀)	−0·0729	−0·0347	0·4167
H(C₁₂)	0·6005	0·1635	0·4162
H(C₁₃)	0·5747	0·0913	0·2978
H(O₁)	0·7562	0·2046	0·0191
H(O₂)	0·3941	0·3361	0·0071
H(H₂O)	0·0525	0·2699	0·4776
H(H₂O)	−0·0365	0·3347	0·4258

only, the same value being assumed for the oxygen and sulphur atoms. The standard deviations obtained are:

C $\sigma(x) = 0·024$ Å $\sigma(y) = \sigma(z) = 0·016$ Å
O $\sigma(x) = 0·024$ $\sigma(y) = \sigma(z) = 0·015$
S $\sigma(x) = 0·024$ $\sigma(y) = \sigma(z) = 0·008$

It is probable that the smaller number of terms used for the refinement of the x coordinates accounts for their lower accuracy. Since most of the atoms are overlapping in the [010] projection (Fig. 4), it is likely that $\sigma(x)$ is an underestimate, at least for the carbon atoms.

The interatomic distances, l, and the valency

Table 3. *Bond lengths in the 4,4'-dihydroxythiobenzophenone molecule*

Bond	l	$\sigma(l)$
S–C(1)	1·64₇ Å	0·02₄ Å
O(1)–C(5)	1·37₉	0·02₅
O(2)–C(11)	1·37₄	0·02₁
C(1)–C(2)	1·52₅	0·02₃
C(1)–C(8)	1·47₇	0·02₁
C(2)–C(3)	1·40₃	0·02₆
C(3)–C(4)	1·36₈	0·02₂
C(4)–C(5)	1·41₇	0·02₄
C(5)–C(6)	1·35₉	0·02₅
C(6)–C(7)	1·37₆	0·02₃
C(7)–C(2)	1·42₈	0·02₃
C(8)–C(9)	1·42₅	0·02₈
C(9)–C(10)	1·42₄	0·02₂
C(10)–C(11)	1·41₁	0·03₁
C(11)–C(12)	1·41₃	0·02₈
C(12)–C(13)	1·40₀	0·02₃
C(13)–C(8)	1·39₀	0·03₁

angles, θ, deduced from the final atomic coordinates, are given in Tables 3 and 4 respectively. Table 3 also shows standard deviations of the bond lengths, $\sigma(l)$, estimated according to the formula of Ahmed & Cruickshank (1953). Using the equation given by Darlow (1960), the standard deviation of the C(2)–C(1)–C(8) valency angle is found to be $\sigma(\theta)=2\cdot3°$.

Table 4. *Valency angles in the 4,4'-dihydroxythiobenzophenone molecule*

Bonds	Angle
S–C(1)–C(2)	$119\cdot5_2°$
C(2)–C(1)–C(8)	$117\cdot2_7$
C(3)–C(2)–C(1)	$121\cdot4_0$
C(1)–C(8)–C(13)	$120\cdot8_1$
O(1)–C(5)–C(4)	$120\cdot8_7$
O(2)–C(11)–C(10)	$117\cdot4_2$
C(7)–C(2)–C(3)	$119\cdot3_8$
C(2)–C(3)–C(4)	$120\cdot8_3$
C(3)–C(4)–C(5)	$118\cdot7_9$
C(4)–C(5)–C(6)	$120\cdot8_7$
C(5)–C(6)–C(7)	$121\cdot5_3$
C(6)–C(7)–C(2)	$118\cdot5_1$
C(13)–C(8)–C(9)	$120\cdot6_2$
C(8)–C(9)–C(10)	$118\cdot3_0$
C(9)–C(10)–C(11)	$119\cdot6_8$
C(10)–C(11)–C(12)	$121\cdot5_3$
C(11)–C(12)–C(13)	$117\cdot9_9$
C(12)–C(13)–C(8)	$121\cdot8_4$

The planarity of that part of the molecule formed by the atoms S, C(1), C(2), C(5), O(1), C(8), C(11), O(2) has been tested by calculating the equation of the best plane through these atoms and also the displacements, Δ, of the individual atoms from this plane (Table 5). The maximum value of Δ is $0\cdot06$ Å, and the root mean square value is $0\cdot033$ Å. Since the estimated standard deviation is $0\cdot034$ Å, this part of the molecule can be considered as planar within the limits of experimental error. The benzene ring (C(2) $\cdots$ C(7)) is rotated out of this plane by about $47°$ and the other ring (C(8) $\cdots$ C(13)) by about $30°$. These two rings are themselves planar within the

Table 5. *Displacements (Δ) from the mean plane*

Atom	Displacement	Atom	Displacement
S	$-0\cdot03$ Å	O(1)	$-0\cdot04$ Å
C(1)	$0\cdot01$	C(8)	$-0\cdot03$
C(2)	$0\cdot06$	C(11)	$0\cdot02$
C(5)	$0\cdot01$	O(2)	$-0\cdot02$

Table 6. *Displacements from the mean planes of the benzene rings*

First ring		Second ring	
Atom	Displacement	Atom	Displacement
C(2)	$-0\cdot01$ Å	C(8)	$-0\cdot01$ Å
C(3)	$0\cdot01$	C(9)	$0\cdot00$
C(4)	$0\cdot01$	C(10)	$0\cdot01$
C(5)	$-0\cdot02$	C(11)	$0\cdot00$
C(6)	$0\cdot01$	C(12)	$-0\cdot01$
C(7)	$0\cdot01$	C(13)	$0\cdot01$

limits of experimental error, as is shown by the displacements of their constituent atoms from their mean planes, listed in Table 6.

Discussion of the structure

The main factor dominating the packing in the crystal lattice of 4,4'-dihydroxythiobenzophenone monohydrate is the hydrogen bonding, as illustrated in Figs. 5 and 6. The hydrogen bond lengths, with their standard deviations and angles, are given in Table 7.
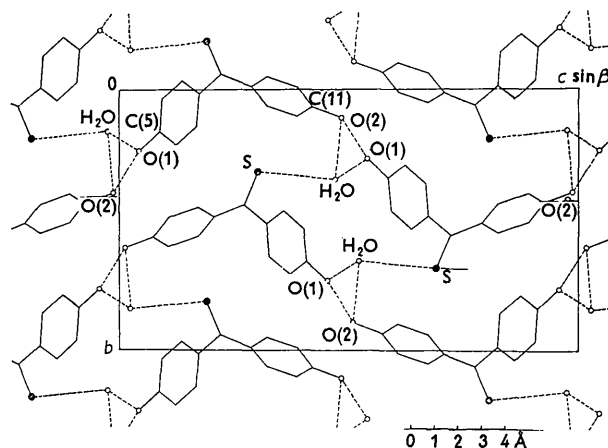

Fig. 5. The view of the structure looking down the a axis. Dashed lines represent the hydrogen bonds.

The structure consists of continuous zigzag chains of organic molecules running parallel to the c direction; within the chains, the molecules are linked together by hydrogen bonds O(1)–H–O(2) between the phenolic groups, but the hydrogen bonds S $\cdots$ H–O expected by Brocklehurst are not present. There are two families of chains, pointing in opposite directions. In the first family, the alternate molecules of a chain are related by the c-glide reflexion plane, $y=\frac{1}{4}$, while the chains of the second family lie on the glide planes $y=\frac{3}{4}$.

Table 7. *Hydrogen bond lengths and angles in crystalline 4,4'-dihydroxythiobenzophenone monohydrate*

Bond	l	$\sigma(l)$
O(2)–O(1)	$2\cdot76_5$ Å	$0\cdot03_0$ Å
O(1)–O(H$_2$O)	$2\cdot69_9$	$0\cdot02_6$
O(H$_2$O)–O(2)	$3\cdot07_1$	$0\cdot02_6$
O(H$_2$O)–S	$3\cdot36_7$	$0\cdot01_7$

Bonds	Angle
S–O(H$_2$O)–O(2)	$85\cdot3_8°$
C(5)–O(1)–O(H$_2$O)	$123\cdot1_1$
C(11)–O(2)–O(1)	$115\cdot2_9$

Hydrogen bonds, O(1)–H–O(H$_2$O) and O(2)–H–O(H$_2$O), from a water molecule to the phenolic group in each of two organic molecules link the chains of
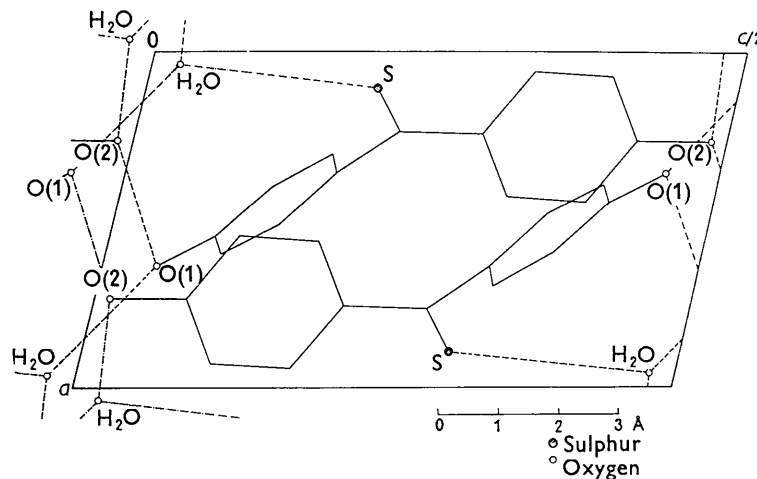
Fig. 6. The view of the structure looking down the b axis. Dashed and dashed-dotted lines represent two sets of hydrogen bonds forming helical chains whose axes lie parallel to the a direction at heights of approximately $b/4$ and $3b/4$ respectively.

a family together; in this way, the three kinds of hydrogen bond between the oxygen atoms of the structure form continuous helical chains parallel to the a direction, the axes of the helices lying approximately along the lines $x\frac{1}{4}0$, $x\frac{3}{4}0$, $x\frac{1}{4}\frac{1}{2}$ and $x\frac{3}{4}\frac{1}{2}$. The bond O(2)–H–O(H$_2$O) is rather long, although it is shorter than some hydrogen bonds that have previously been reported between oxygen atoms (Yakel & Hughes, 1954).

A sulphur atom is located at $3\cdot37\pm0\cdot02$ Å from the oxygen atom of a water molecule in a direction which satisfies the angular requirements for a hydrogen bond as given by Donohue (1952) and Fuller (1959). It is therefore likely that a weak hydrogen bond exists between the water of crystallization and a sulphur atom, forming a cross-linkage between the molecular chains of the different families.

An analysis of all interatomic distances shorter than 4 Å showed that all intermolecular contacts other than those listed in Table 7 have the normal van der Waals separation. A more accurate determination of bond lengths and angles was not possible owing to the overlapping of atoms in the [010] projection.

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References

AHMED, F. R. & CRUICKSHANK, D. W. J. (1953). *Acta Cryst.* **6**, 385.

BERGHUIS, J., HAANAPPEL, IJ, M., POTTERS, M., LOOPSTRA, B. O., MACGILLAVRY, C. H. & VEENENDAAL, A. L. (1955). *Acta Cryst.* **8**, 478.

BROCKLEHURST, P. (1956). Ph. D. Thesis, Manchester University.

CRUICKSHANK, D. W. J. (1949). *Acta Cryst.* **2**, 154.

CURTIS, A. R. (1959). AERE–R 3134.

DARLOW, S. F. (1960). *Acta Cryst.* **13**, 683.

DONOHUE, J. (1952). *J. Phys. Chem.* **56**, 502.

FORSYTH, J. B. & WELLS, M. (1959). *Acta Cryst.* **12**, 412.

FULLER, W. (1959). *J. Phys. Chem.* **63**, 1705.

HANSON, A. W., LIPSON, H. & TAYLOR, C. A. (1953). *Proc. Roy. Soc.* A, **218**, 371.

JELLINEK, F. (1958a). *Acta Cryst.* **11**, 626.

JELLINEK, F. (1958b). *Acta Cryst.* **11**, 677.

MCWEENY, R. (1951). *Acta Cryst.* **4**, 513.

TAYLOR, C. A. & MORLEY, K. A. (1959). *Acta Cryst.* **12**, 101.

VIERVOLL, H. & ØGRIM, O. (1949). *Acta Cryst.* **2**, 277.

WILSON, A. J. C. (1942). *Nature, Lond.* **150**, 152.

WOOLFSON, M. M. (1957). *Acta Cryst.* **10**, 116.

YAKEL, H. L. & HUGHES, E. W. (1954). *Acta Cryst.* **7**, 291.