

The Crystal Structure of Phloroglucinol Dihydrate

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Crystals of phloroglucinol dihydrate are orthorhombic, space group $Pnma$, with cell dimensions $a = 6.73$, $b = 13.58$, $c = 8.09$ Å. This cell contains four molecules of phloroglucinol and eight molecules of water. A trial structure, which differs from that postulated by Banerjee & Ahmad, has been refined by Fourier projections. It consists of corrugated layers of phloroglucinol molecules linked through water molecules by hydrogen bonds of lengths 2.74–2.88 Å. The layers are weakly bound to each other by fewer hydrogen bonds of length 2.74 Å between pairs of water molecules. The average dimensions within each phloroglucinol molecule are C–C = 1.41 Å, C–OH = 1.36 Å, in good agreement with the electron-diffraction values of Sanengen. Diffuse X-ray scattering is interpreted in terms of thermal motion of the molecules and a disorder effect in which some parts of the structure are displaced by approximately $\frac{1}{2}a$ relative to the rest.

Introduction and previous work

In the crystal structures of polyhydroxy compounds the tendency to form the maximum complement of hydrogen bonds may not be easy to reconcile with the tendency to adopt a closely packed molecular arrangement. This is particularly true in the case of polyhydric phenols, where the component molecules are rigid and therefore cannot assist in effecting the compromise by undergoing major distortions. The structure of polyhydric phenols may therefore be expected to show unusual features. In the case of quinol, one of the fully hydrogen-bonded arrangements of molecules is so open that it gives rise to a series of molecular compounds of special interest (Palin & Powell, 1948). It was because there might be some parallel behaviour in structures involving the related molecule phloroglucinol that the crystal structure of phloroglucinol dihydrate has been determined.

Crystal constants for the substance are recorded in Groth (1917), and further information on optical properties is given by Winchell (1954). A previous X-ray examination by Banerjee & Ahmad (1938) gave a cell having $a = 6.79$, $b = 8.10$, $c = 13.70$ Å and containing four molecules of formula $C_6H_3(OH)_3 \cdot 2H_2O$. These authors gave for the space group $Pn\bar{m}$, and some suggestions were made concerning the structure. Bose & Sen (1943) re-determined the cell dimensions as $a = 6.740$, $b = 8.090$, $c = 13.604$ Å, and gave axial ratios derived from new goniometric measurements. These agree with their X-ray measurements and are somewhat different from those given in Groth. Chorgade (1943) found the cell dimensions 6.75, 8.10 and 13.51 Å and deduced that the space group is Pna or $Pnam$. Sanengen (1943), from electron-diffraction

studies of the vapour of phloroglucinol, reports molecular dimensions C–C = 1.40, C–OH = 1.36 Å.

Experimental

Phloroglucinol dihydrate A. R. was recrystallized from water and so obtained as crystals suitable for X-ray examination. Oscillation and Weissenberg photographs were obtained with Cu K radiation, with the principal axes taken in turn as oscillation axis. Relative F values for $0kl$ and $h0l$ were determined from visual estimates of intensities on Weissenberg photographs, the required intensity range being covered by use of long and short exposures and the multiple-film technique.

Cell dimensions and space group

From high-order reflexions on films bearing fiducial marks the unit-cell dimensions derived were

$$a = 6.73 \pm 0.01, \quad b = 13.58 \pm 0.02, \quad c = 8.09 \pm 0.01 \text{ Å}.$$

From these and the density 1.46 g.cm.⁻³ it is found that there are 4 molecules per unit cell (calculated density = 1.457 g.cm.⁻³). The systematic absences, determined from Weissenberg photographs, are $0kl$ when $k+l$ is odd, $hk0$ when h is odd. These restrict the space group to $Pnma$ or $Pn2a$. The b and c axes have been interchanged compared with those of previous workers. When allowance is made for this change of axes, the present observations disagree with those of Banerjee & Ahmad, but are in agreement with those of Chorgade.

The centrosymmetric space group $Pnma$ was considered by Chorgade and rejected for reasons given

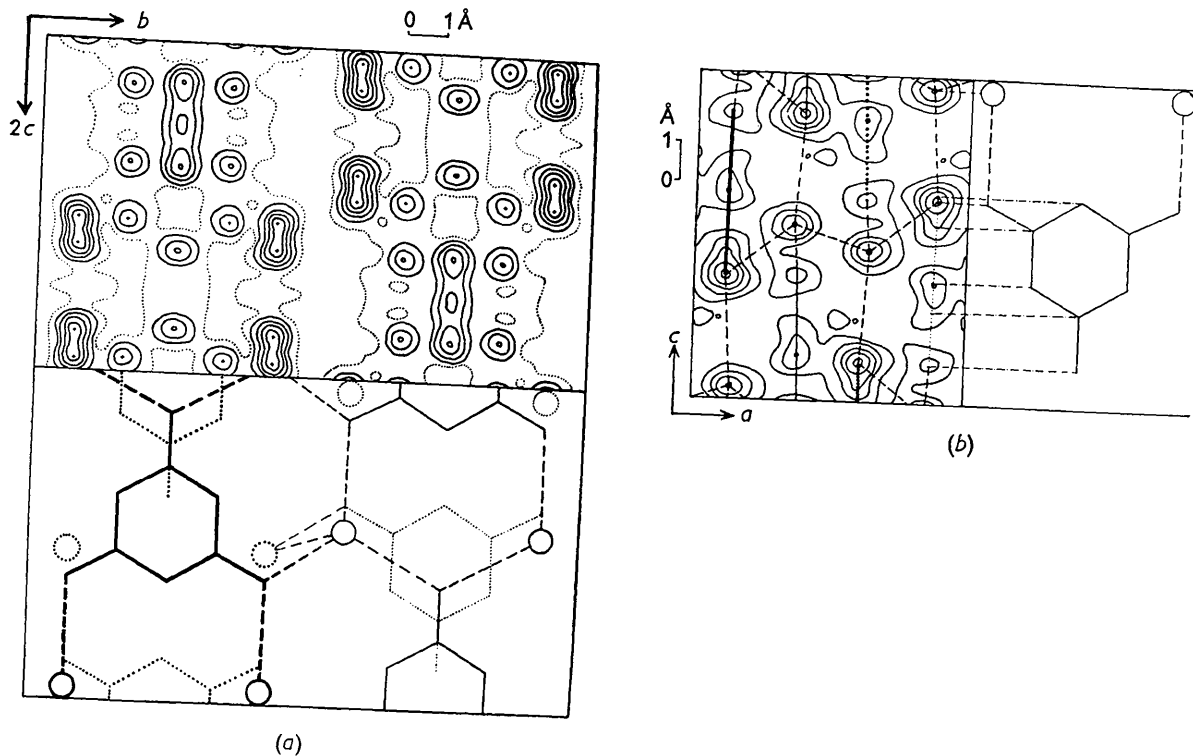


Fig. 1. (a) Electron-density projection on (100). Contours at 2, 4, 6, ... $e.\text{Å}^{-2}$. In the lower part of the diagram, phloroglucinol molecules are shown in skeleton form by lines: heavy full line at $x = \frac{1}{4}$, light full line at $x = \frac{3}{4}$, heavy dotted line at $x = \frac{1}{2}$, light dotted line at $x = \frac{1}{2}$. Broken lines indicate hydrogen bonds. Circles represent water molecules. (b) Electron-density projection on (010). Contours at 5, 10, 15, ... $e.\text{Å}^{-2}$. Phloroglucinol molecules have their planes parallel to the line of sight in this projection, those at $y = \frac{1}{4}$ being represented by heavy full lines and heavy dotted lines, and those at $y = \frac{3}{4}$ by light full lines and light dotted lines. The appearance of the molecules in one layer is compared, in the right-hand part of the diagram, with their appearance in the (100) projection.

below. In this space group four equivalent molecules must have a symmetry centre or a plane of symmetry. The phloroglucinol molecule has no symmetry centre. If it makes use of one of its planes of symmetry, only those orientations which bring the plane of the benzene ring nearly parallel to (100), and perpendicular to the plane of symmetry of the structure, are compatible with the optical and magnetic anisotropy, and with some of the X-ray data. This part of the argument is considered correct, and in the present investigation has been confirmed by packing considerations which also require the same arrangement with a plane of symmetry of the structure perpendicular to the benzene ring and passing through one of the three OH groups of the molecule. Chorgade, assuming that the molecules lie in the plane (100) or in the glide plane parallel to it, expected the systematic absence of certain reflexions, contrary to observation, and therefore rejected this space group in favour of *Pna*. This reasoning does not apply if, as the space group permits, the molecules have x coordinates other than $0, \frac{1}{2}, \frac{1}{4}, \frac{3}{4}$. No pyroelectric effect has been observed and no other evidence of non-centrosymmetric character has been found. Accordingly, in the present investigation the centrosymmetric space group was used

as a basis and the choice is justified by the resulting electron-density maps.

Analysis of the structure

Provisional positions for the atoms were determined as follows. The strong negative birefringence, with α parallel to a , and the good cleavage parallel to (100) suggest a structure of some form of layers parallel to (100). Chemical considerations, supported by the hardness of the crystals, observed directly and revealed in the intense nature of high-order reflexions, suggest that hydrogen bonds play an important role in the structure.

Four phloroglucinol molecules in special positions linked by hydrogen bonds through eight water molecules in general positions were found by a trial model to give a satisfactory structure. With this, sufficient agreement was obtained between calculated and observed F values to make possible a determination of the signs of $F(0kl)$. Successive approximations then led to the electron-density map shown in Fig. 1(a). In this, most of the atoms of the phloroglucinol molecules are resolved and the positions of the molecules

are made clear. The water molecules, however, are not resolved owing to their proximity in projection to OH groups.

From the y, z parameters so obtained, and from consideration of the trial structure, a set of x parameters was derived and used in a similar procedure to obtain the electron-density projection on (010), as shown in Fig. 1(b). In this projection the phloroglucinol molecule is represented by three peaks corresponding to groups of overlapping atoms. Only its general position is shown, but x values may be derived from the observed tilt of the molecule, assumed to be planar, and the known z parameters of its atoms. The positions of the water molecules are shown by clearly resolved peaks, each of which represents two water molecules having identical x and z parameters.

A complete list of coordinates derived from the two projections is given in Table 1. The z values are mainly

Table 1. *Final atomic parameters*

Atom	x/a	y/b	z/c
C ₁	0.383	0.250	0.218
C ₂	0.385	0.160	0.128
C ₃	0.388	0.160	-0.043
C ₄	0.390	0.250	-0.137
O ₁	0.380	0.250	0.383
O ₂	0.390	0.071	-0.122
O ₃	0.863	0.071	-0.038

derived from the (100) projection, but those for O₂ and O₃ are taken from the (010) projection because of better resolution.

The comparison of calculated and observed F values shown in Table 2 gave $\Sigma(|F_o| - |F_c|) \div \Sigma|F_o|$ values of 23% (0kl) and 26% (h0l). Both these figures of merit are adversely affected by the disorder discussed below. Interatomic distances and bond angles, as calculated from the parameters, are shown in Fig. 2. No signifi-

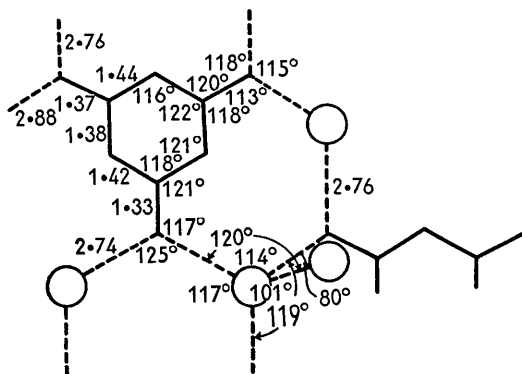


Fig. 2. Part of the structure, showing interatomic distances (in Å) and bond angles. Estimated error in bond lengths is ± 0.05 Å, and in bond angles is $\pm 3^\circ$.

cance is attached to the slight departures of the benzene ring from regular hexagonal form. The mean C-C distance is 1.41 Å and the mean C-OH is 1.36 Å. Electron-diffraction values of Sanengen were 1.40 and 1.36 Å.

Description of the structure

Between OH groups and water molecules there are various distances between 2.74 and 2.88 Å, all representing hydrogen bonds. The distance 2.74 Å between two water molecules is also a hydrogen bond length and may be compared with the value 2.76 Å observed in ice. The hydrogen bond distances shown are those calculated for the ideal structure represented by the parameters in the table, but in the real structure somewhat different distances may result locally owing to disorder effects. The whole structure may be described as a set of layers of the form shown in Fig. 3. The phloroglucinol molecules are linked through

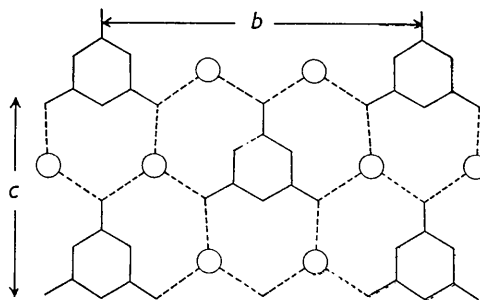


Fig. 3. One hydrogen-bonded layer of the structure, as seen in projection on (100). Circles represent water molecules.

water molecules by hydrogen bonds, each OH group having two hydrogen bonds and each water molecule linking to three OH groups. This gives six hydrogen bonds for each $C_6H_3(OH)_3 \cdot 2H_2O$, i.e. one less than the number of hydrogen atoms available. A seventh hydrogen bond is formed between a pair of water molecules in different layers, i.e. when the whole structure is considered there is one hydrogen bond for each hydrogen atom that is linked to oxygen. The layers of the type shown in Fig. 3 are not flat, some of the hydrogen bonds linking the molecules being inclined to the plane of the figure so that all four phloroglucinol molecules in one cell are at different heights. The molecule at $x \approx \frac{1}{3}$, together with that at $x \approx \frac{2}{3}$, forms one corrugated layer; a similar layer is formed by corresponding molecules at $x \approx \frac{5}{6}$ and $x \approx \frac{7}{6}$. The layers are bound to each other by the hydrogen bonds between pairs of water molecules, and since there are only four such links per unit cell they are at comparatively large distances apart and the binding between the layers is therefore weak. The water molecules appear in the structure as a linked group $2H_2O$, similar to that found by Andersen & Hassel (1948) in phloroglucitol dihydrate.

Thermal and disorder effects

On many of the X-ray photographs two effects additional to the Bragg reflexions could be seen. These were diffuse thermal reflexions and disorder streaks.

Table 2. Comparison of observed and calculated structure factors

(The values are one-eighth of the absolute scale)

<i>hkl</i>	F_c	F_o	<i>hkl</i>	F_c	F_o	<i>hkl</i>	F_c	F_o
002	+6.30	3.52	075	+1.82	2.00	602	+0.37	< 0.7
004	-4.40	3.42	095	-0.13	< 0.5	702	-0.93	< 0.7
006	0.00	< 0.7	0,11,5	-0.93	1.57	802	+0.71	< 0.6
008	+1.67	2.02	0,13,5	+0.10	< 0.4	103	+5.42	4.68
0,0,10	-1.04	1.09	0,15,5	+0.73	0.44	203	-4.01	4.57
020	-3.32	3.25	026	+0.15	< 0.7	303	-3.31	3.34
040	-0.69	1.17	046	-0.24	< 0.6	403	-0.31	< 0.7
060	-5.95	6.25	066	+0.19	< 0.6	503	-1.89	1.45
080	-2.38	3.06	086	-0.53	< 0.5	603	+1.13	1.05
0,10,0	-5.20	4.23	0,10,6	+0.02	< 0.4	703	+0.77	< 0.7
0,12,0	+4.59	4.36	0,12,6	0.00	< 0.4	803	+0.21	< 0.6
0,14,0	+0.88	0.91	0,14,6	+0.09	< 0.3	104	-0.19	< 0.9
0,16,0	+0.86	0.44	017	+2.11	1.57	204	-1.12	1.58
011	-2.22	1.26	037	+0.04	< 0.5	304	+0.45	1.74
031	+7.03	5.31	057	-0.18	0.87	404	+2.20	2.42
051	+2.74	3.25	077	+0.30	0.60	504	+0.53	< 0.7
071	+0.57	0.59	097	+0.33	0.66	604	+1.16	0.64
091	-2.67	3.32	0,11,7	-1.41	1.09	704	-0.45	0.64
0,11,1	-0.22	0.47	028	-0.49	0.44	105	+1.20	2.00
0,13,1	-1.09	1.15	048	+0.31	0.44	205	-2.20	3.30
0,15,1	+0.47	0.62	068	-0.71	0.78	305	-0.82	1.32
0,17,1	+0.59	0.31	088	+0.10	< 0.4	405	+0.43	< 0.8
022	+3.15	2.94	0,10,8	-0.75	0.80	505	-0.73	< 0.7
042	-3.30	2.90	019	+0.79	0.90	605	+0.86	0.83
062	-0.03	0.91	039	+1.01	1.01	705	+0.22	< 0.6
082	-2.71	3.56	059	+1.40	1.58	106	-2.18	3.42
0,10,2	-0.62	1.17	079	-0.32	0.65	206	-0.04	< 0.8
0,12,2	+0.82	0.75	0,2,10	-0.14	< 0.3	306	-1.43	2.04
0,14,2	+1.08	0.98	0,4,10	+0.56	0.87	406	+0.01	< 0.7
0,16,2	-0.11	< 0.3				506	+1.07	0.83
013	+2.50	2.25	200	+1.62	1.24	606	+0.06	< 0.6
033	+4.53	4.06	400	-11.00	8.35	107	-1.23	1.25
053	+3.37	3.56	600	-1.16	0.82	207	-2.23	2.33
073	-0.17	< 0.7	800	+2.57	1.32	307	+0.65	0.89
093	-1.71	2.16	101	-4.21	3.81	407	+0.24	< 0.7
0,11,3	-1.66	2.02	201	-0.71	1.24	507	+0.63	< 0.6
0,13,3	-0.54	0.41	301	-0.14	0.98	607	+1.14	0.80
0,15,3	+0.25	0.29	401	-0.15	1.20	108	-0.37	< 0.7
024	+1.75	1.74	501	+2.39	1.97	208	+0.33	< 0.7
044	-0.64	0.99	601	+0.08	< 0.7	308	0.00	< 0.7
064	+1.04	2.02	701	+0.70	< 0.7	408	-1.18	1.14
084	-0.38	< 0.6	801	+0.11	< 0.6	508	+0.54	< 0.6
0,10,4	+1.33	1.37	102	+2.28	3.11	109	-0.47	1.09
0,12,4	-1.10	1.57	202	-0.55	1.50	209	-1.35	1.37
0,14,4	+0.18	< 0.4	302	+2.70	2.53	309	+0.46	0.64
015	+1.87	2.12	402	-2.64	2.18	409	-0.04	< 0.6
035	+1.52	1.10	502	+0.07	< 0.8	1,0,10	0.00	< 0.6
055	-2.52	1.85				2,0,10	+0.12	< 0.6

Some of these have been observed and discussed by Datta (1951).

Among the diffuse thermal reflexions observed the most prominent are those in the neighbourhoods of the Bragg reflexions 210, 230 and 250. These are in the form of patches which become more elongated along the direction parallel to a^* as the k index increases, and correspond to what might be expected from the structure as determined. The atoms of each phloroglucinol molecule are in planes approximately parallel to (200) and, when the corrugated layers are considered as a whole, a number of atoms are seen to lie approximately in planes parallel to (210) with the rather widely spaced hydrogen bonds roughly perpendicular to these planes. Atomic vibrations perpen-

dicular to these layers may be expected to be more pronounced than in other directions.

In addition to these diffuse reflexions, effects clearly due to disorder in the structure are observed. All crystals do not show the disorder effect to the same degree, and some X-ray photographs with small crystals show no evidence of it. Usually photographs obtained by oscillating the crystal about the b axis show on some row lines streaks which reach from one layer line to the next, or further. For oscillation about the c axis, streaks parallel to the layer lines are found. When a is the oscillation axis, streaks parallel to the layer lines are very prominent for odd-order layers, although traces are also observed on the second layer. The fourth layer line on the extreme edge of the film

consists of a few ordinary reflexions, and has no streaks.

The zero-layer Weissenberg photograph about [100] is normal but the first layer has, in addition to $1kl$ reflexions, a set of streaks more or less continuous along lines of constant l , i.e. in the streaks the k index is variable and non-integral. A zero-layer Weissenberg photograph about [001] shows streaks along lines of constant h , i.e. in the streaks k is again variable and non-integral. In this photograph the streaks are less pronounced and occur near the reflexions 210, 400 (both very strong) and 220 (weak).

These effects are attributed to a disorder arising from the hydrogen bonding.

Running through the structure parallel to (010) there are sheets of oxygen atoms. These are made up of water molecules and OH groups of phloroglucinol molecules whose planes are perpendicular to these oxygen sheets. Each phloroglucinol molecule contributes two OH groups, one on either side, as components of two such parallel sheets. Each sheet is linked by hydrogen bonds to an adjacent similar sheet. The oxygen atoms of a sheet are shown in Fig. 4(a) by

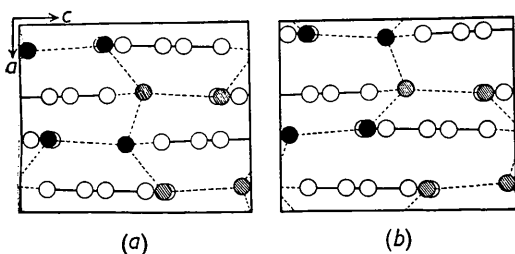


Fig. 4. (a) The normal structure, as seen in projection on (010) (cf. Fig. 1(b)). (b) The structure, after displacement through approximately $\frac{1}{2}a$, of the structural sheet containing the oxygen atoms represented by the full circles.

full circles and those of the adjacent sheet by shaded circles, and the hydrogen bond system is indicated. The open circles represent the carbon atoms and CH groups of the projected phloroglucinol molecules and the OH groups which do not form part of the sheets of oxygen atoms just described.

The whole structure is formed by sheets attached to each other in this way. It happens that an OH group and a water molecule have about the same z coordinates and differ in their x coordinates by approximately $\frac{1}{2}a$. It is thus possible for the structure to grow by attachment of these parallel sheets in a manner which does not correspond to the supposed space-group symmetry. If the sheet to be attached is displaced by nearly $\frac{1}{2}a$, as shown in Fig. 4(b), every oxygen atom will come to a position in which it may form a hydrogen bond with an oxygen atom of the sheet below. In this process OH groups take up approximately the positions that should be occupied by H_2O , and vice versa, and a different set of hydrogen bonds is formed.

Displacement of the structural sheets brought about in this way would give rise to X-ray reflexions with non-integral values of k , and the extension of reciprocal-lattice points along directions parallel to b^* should occur for all planes other than those parallel to the disorder displacement, i.e. for all reflexions except $0kl$. This is in agreement with the observations. The displacement of almost $\frac{1}{2}a$ explains the weakness of the streaks on the second layer line of a -axis oscillation photographs compared with those on the first and third layers, since a displacement of exactly $\frac{1}{2}a$ would give no disorder streaks for reflexions having $h = 2$.

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