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The Crystal and Molecular Structure of Phloroglucinol*

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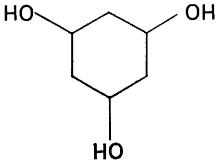
Crystals of phloroglucinol are orthorhombic, spacegroup $P2_12_12_1$, with cell dimensions 4·83, 9·37, 12·56 Å. The unit cell contains four molecules. All hydroxyl-hydrogen atoms are involved in hydrogen bonding. The $OH \cdots O$ distances are of normal length, 2·75 Å. The hydrogen bonds form infinite helices around the screw axes parallel to the *b* axis. The average bond distances within the molecule are C–C = 1·38 Å and C–OH = 1·37 Å. The benzene ring appears to deviate slightly from a regular hexagon.

Introduction

The crystal structure of phloroglucinol dihydrate has been determined by Wallwork & Powell (1957). Their introductory arguments induced the author to undertake the present investigation. Originally in this work only the determination of the arrangement of the hydrogen bonding was intended, but as the work proceeded a more accurate investigation seemed to be worth while as some unexpected details concerning the stereochemistry of the phloroglucinol (1,3,5-trihydroxybenzene) molecule (I) became apparent.



(I)

Experimental

Single crystals suitable for X-ray diffraction were obtained from the wall of a glass tube where they deposited by sublimation under vacuum. The lower part of the tube containing the previously dried substance was immersed in an oil bath kept at 160 – 180 °C, whereby crystals formed just above the surface level of the oil. Two to three hours sufficed to grow crystals of suitable size.

The unit-cell dimensions and systematic absences were determined from oscillation and Weissenberg photographs of crystals mounted along the shortest and next shortest principal axes. Cu $K\alpha$ radiation was used for these as well as for all intensity recordings.

Orthorhombic $a = 4{\cdot}83 \pm 0{\cdot}01$ Å
$b = 9{\cdot}37 \pm 0{\cdot}02$
$c = 12{\cdot}56 \pm 0{\cdot}03$

Density, experimental	1·46 g.cm^{-3}
Density, calculated	1·47 g.cm^{-3}
Molecules per unit cell,	4
Absorption coeff. calc.	11·8 cm^{-1}
Systematic absences:	*h*00 when *h* odd 0*k*0 when *k* odd 00*l* when *l* odd
Space group	$P2_12_12_1$

To protect the crystals from moisture in the air, they were mounted in thin-walled Lindemann-glass tubes. Crystals having cross sections less than 0·2 mm were used for the recording of intensities on integrated Weissenberg films using the multiple film technique. The 0*kl*, 1*kl*, 2*kl* and *h*0*l*, *h*1*l*, *h*2*l*, *h*3*l*, *h*4*l* layers were recorded and the relative intensities measured with a photometer, some weaker ones being estimated visually. There are 577 independent possible reflexions in the Cu $K\alpha$ reciprocal sphere; of these, 95 were found below the observed intensity minimum.

Structure analysis

No corrections apart from the usual Lorentz and polarization factors were applied to the intensities. To correlate the different layers scaling factors were calculated from structure amplitude ratios of common reflexions in the 0–2, *kl* and *h*, 0–4, *l* sets.

As the 0*kl* reflexions are consistently weak when *l* is odd, the (100) projection, plane group *pgg*, is pseudo *pmg* with the pseudo mirror line parallel to the *c* axis. This implies that in projection one oxygen atom, the carbon atom to which it is bonded and the corresponding *para* carbon atom all lie close to the glide parallel to the *c* axis. From a Patterson synthesis of the same projection a satisfactory solution was found. The position of the molecule in the (010) projection was found from the coordinates known from the (100) projection and the assumption of normal hydrogen bond lengths between neighbouring oxygens of different molecules.

Coordinates from Fourier maps of the two projections were used as starting values in a three-dimensional least-squares refinement (Rutten, 1963), normalizing

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the relative structure amplitudes to give the best fit with the calculated ones. The scattering factors of Cromer, Larson & Waber (1963) were used.

The hydrogen atoms were included at an early stage in the refinement with likely thermal parameters, but these were not allowed to vary before the last iterations. The refinement is based on 479 intensities, the 95 intensities observed with zero intensity and the three strongest intensities were left out.

The final atomic positional and thermal parameters are given in Table 1.

The interatomic distances and bond angles are given in Fig. 1 and Table 2.

Discussion

Sandengen (1943) has studied phloroglucinol in the vapour phase by electron diffraction and found the bond lengths C–C = 1·40 Å, C–OH = 1·36 Å. The C–C distances found here are somewhat shorter and the C–OH somewhat longer than these, but this is hardly significant. More apparent is the distortion of the benzene ring. This is not found to be a regular hexagon, all internal angles at carbons bonded to oxygen being significantly larger than the other three angles. A similar distortion in symmetrically substituted benzene is reported by Hanson (1964).

The equation for the plane fitted by least squares to the carbon positions is

$$0{\cdot}7602X+0{\cdot}0388\,Y+0{\cdot}6485Z-5{\cdot}5901=0\,.$$

The deviations from this plane are +0·010, −0·014, +0·012, −0·004, −0·001 and −0·002 Å; the carbon positions thus do not deviate significantly. The oxygen atoms on the other hand cannot be considered to be coplanar with the benzene ring, their distances from the plane being +0·024, +0·039 and +0·045 Å.

The distances between neighbouring oxygen atoms of different molecules are about equal and correspond to normal hydrogen bonds. The hydrogen bonds form helices around the screw axes parallel to the b axis. Assuming the hydrogen atoms to lie near the connect-

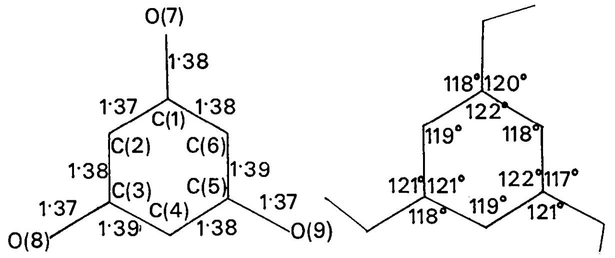

Fig. 1. Interatomic distances and bond angles.

Table 1. *Final parameters*

	x/a	y/b	z/c	B	U_{11}	U_{22}	U_{33}	$2U_{12}$	$2U_{23}$	$2U_{31}$
C(1)	0·4082	0·4929	0·4815		236	153	188	−31	30	78 Å^{2}10^{-4}
C(2)	0·5106	0·3693	0·4379		264	135	309	−51	63	19
C(3)	0·6993	0·3786	0·3556		250	131	301	−6	−25	56
C(4)	0·7758	0·5097	0·3133		339	190	312	−67	−35	171
C(5)	0·6660	0·6318	0·3578		292	95	256	−46	0	66
C(6)	0·4792	0·6255	0·4421		290	134	262	36	14	159
O(7)	0·2251	0·4810	0·5659		374	164	315	−62	−13	240
O(8)	0·8150	0·2582	0·3121		420	132	412	100	−38	268
O(9)	0·7424	0·7647	0·3230		429	129	357	−38	11	207
H	0·4724	0·2763	0·4645	1·3 Å^2						
H	0·9306	0·5057	0·2665	0						
H	0·3993	0·7115	0·4872	2·0						
H	0·2633	0·5577	0·6160	3·5						
H	0·7849	0·1549	0·3749	7·6						
H	0·8502	0·7625	0.2695	2·0						

Standard deviations		x	y	z
	C	0·0058	0·0047	0·0053 Å
	O	0·0043	0·0034	0·0037
	H	0·080	0·080	0·080

$$\Sigma\,|F_c|-|F_o|\,/\Sigma|F_c|=0{\cdot}075$$

Table 2. *Interatomic distances and bond angles*

C(2)–C(4)	2·41 Å	C(1)–C(3)	2·37 Å
C(4)–C(6)	2·42	C(3)–C(5)	2·38
C(6)–C(2)	2·41	C(5)–C(1)	2·38

Standard deviations: C–C, 0·007 Å; C–O, 0·006 Å; ∠CCO, 0·5°; ∠CCC, 0·5°.

O(7)–O(8″)	$(\frac{1}{2}+x-1,\ \frac{1}{2}-y,\ \bar{z}+1)$	2·75 Å	∠C(1)–O(7)–O(8″)	113°
O(8)–O(7′)	$(\frac{1}{2}+x,\ \frac{1}{2}-y,\ \bar{z}+1)$		∠C(3)–O(8)–O(7′)	112
O(7)–O(9′)	$(\frac{1}{2}+x-1,\ \frac{1}{2}-y+1,\ \bar{z}+1)$	2·76	∠C(1)–O(7)–O(9′)	107
O(9)–O(7″)	$(\frac{1}{2}+x\ \ \frac{1}{2}-y+1,\ \bar{z}+1)$		∠C(5)–O(9)–O(7″)	128
O(8)–O(9″)	$(\bar{x}+2,\ \frac{1}{2}+y-1,\ \frac{1}{2}-z)$	2·73	∠C(3)–O(8)–O(9″)	126
O(9)–O(8′)	$(\bar{x}+2,\ \frac{1}{2}+y,\ \frac{1}{2}-z)$		∠C(5)–O(9)–O(8′)	113

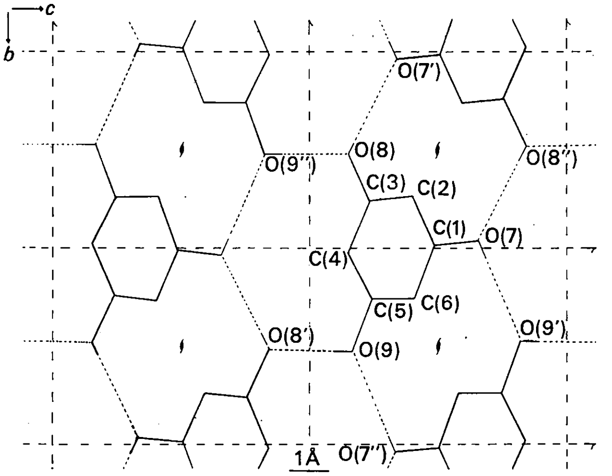

Fig. 2. Arrangement of molecules viewed down the a-axis. Broken lines indicate hydrogen bonds. O(7′) belonges to a molecule one repeat distance above the molecule of O(8″). Similarly O(7″) belongs to a molecule one repeat distance above the molecule of O(9′).

ing line between neighbouring oxygen atoms then in accordance with the valency angle of oxygen the donor-acceptor direction in the helices is likely to be as indicated in Fig. 2.

As mentioned above, the three oxygen atoms of the molecule are all found on the same side of the plane of the benzene ring. This may be related to the situation that the six neighbouring oxygen atoms to which these three are linked by hydrogen bonding are also found on this same side of the plane. As there are no short intermolecular distances in the direction normal to the plane of the benzene ring, the non-planarity of the molecule as a whole (considering carbon and oxygen atoms only), may be due to internal conditions rather than to external ones.

An analysis of the parameters describing the anisotropic thermal motion shows that the largest axes of the vibrational ellipsoids are roughly perpendicular to the plane of the molecule.

On request, a list of structure amplitudes is available from the author.

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The Crystal Structure of Osmium Tetroxide

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Crystals of OsO_4 are monoclinic, space group $C2/c$, with 4 molecules in the cell with dimensions

$a=9{\cdot}379$, $b=4{\cdot}515$, $c=8{\cdot}632$ Å; $\beta=116{\cdot}6°$.

By least-squares refinement of three-dimensional X-ray diffraction data the molecules are tetrahedral with Os–O = 1·74 Å (uncorrected for thermal motion). The molecular arrangement is approximately cubic closest packing. The intermolecular O–O distances exceed 2·98 Å and are consistent with weak intermolecular forces indicated by the high vapor pressure and low melting point.

Introduction

The crystal structure of osmium tetroxide was investigated previously by X-ray photographic methods (Zalkin & Templeton, 1953), but oxygen positions were not determined from the intensity data. The complete structure has now been established with intensity data from the direct counting technique. The new study shows that the old unit cell must be doubled and that the wrong space group had been chosen.

Experimental

Crystals of OsO_4 were grown in sealed glass capillaries by sublimation at room temperature. Raw crystals were obtained from A. D. Mackay, Inc. Rotation, oscillation