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The Crystal Structure of the Molecular Compound formed by Quinol and Acetone

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Crystals of the quinol acetone complex are monoclinic, space group $C2/c$, with a cell of dimensions $a = 18{\cdot}64$, $b = 7{\cdot}14$, $c = 7{\cdot}41$ Å, $\beta = 111°$, containing 4 molecules of quinol and 4 molecules of acetone. A trial structure obtained by Fourier transform and Patterson methods has been refined by Fourier projections. It consists of infinite chains of alternate quinol and acetone molecules in which hydrogen bonds of length 2·74 Å link OH groups of two quinol molecules to each acetone oxygen atom. Adjacent chains are held together by van der Waals forces. The dimensions found for both molecules differ slightly from the values reported by Palin & Powell (1947) for quinol, and by Kimura & Kurita (1951), Allen, Bowen, Sutton & Bastiansen (1952) and Romers & Creutzberg (1956) for acetone.

Introduction

Quinol $HO–C_6H_4–OH$ shows a marked tendency to form crystalline molecular complexes, and this is probably due to the difficulty of satisfying the requirements of both hydrogen bonding and economical packing when quinol crystallizes alone. Evidence for this difficulty is found in the complexity of the incompletely known structure of the usual α form (Powell, 1948) and the instability of the simpler γ structure formed by sublimation (Wallwork, 1950). The β form of quinol has a very open structure which encloses small molecules whenever possible, giving a series of clathrate compounds (Palin & Powell, 1948).

The complex with acetone, $(CH_3)_2.CO$ was known not to be one of the β-quinol clathrate series in view of its 1:1 composition reported by Habermann (1884) and Schmidlin & Lang (1910), and its structure was investigated in order to establish whether complex formation takes place by some other method of enclosure, or by hydrogen bonding involving the acetone itself.

Experimental

Crystals of the complex suitable for X-ray examination were deposited when concentrated solutions of quinol in acetone were cooled slowly. Because the complex is unstable in air, crystals for X-ray examination were sealed in thin-walled Pyrex capillary tubes. Oscillation and zero and first layer Weissenberg photographs were obtained with Cu $K\alpha$ radiation, with the [101], b and c axes taken in turn as oscillation axes. Relative intensities of reflexions on zero layer Weissenberg photographs were determined photometrically by the method of Wallwork & Standley (1954). This method makes some correction for the background intensity on the films, and this was particularly necessary in this case because the crystals were photographed in glass tubes. The required intensity range was covered by the use of long and short exposures, and the multiple-film technique. It was considered unnecessary to make any correction for absorption, because of the small size and the nearly cylindrical cross-sections of the crystals.

Cell dimensions and space group

From high order reflexions on Weissenberg films, the unit-cell dimensions were calculated to be

$$a = 18{\cdot}64\pm0{\cdot}04,\ b = 7{\cdot}14\pm0{\cdot}02,\ c = 7{\cdot}41\pm0{\cdot}02\ \text{Å};\ \beta = 111°\pm1°.$$

The density was obtained by flotation, using a centrifuge to accelerate the movement of the crystals. Since the crystals decomposed fairly quickly in the liquids used, an accurate density could not be obtained. The best value from rapid determinations was 1·21 g.cm.$^{-3}$. This corresponds to 4 quinol and 4 acetone molecules per unit cell (calculated density 1·216 g.cm.$^{-3}$).

The systematic absences determined from zero and first layer Weissenberg photographs are: hkl absent when $h+k = 2n+1$, $h0l$ absent when $h = 2n+1$ or $l = 2n+1$ and $0k0$ absent when $k = 2n+1$. These restrict the space group to Cc or $C2/c$. No pyro-electric effect was observed, and the statistical test (Howells, Phillips & Rogers, 1950) indicated the centrosymmetric space group. 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.

Trial structure

Provisional positions for the atoms were determined as follows. Since there are 4 of each molecule per cell, they must all occupy special positions. An attempt was first made to determine the positions of the quinol molecules. Of the five sets of special positions given in the *International Tables* (1952), (*a*) and (*b*) are improbable, since they would involve quinol molecules stacked parallel to each other, and the symmetry requirements of (*e*) would imply a molecular orientation which is not consistent with that found approximately as described below. Positions (*c*) and (*d*) remain, and these are identical except for a shift of origin of $\frac{1}{2}c$. The quinol molecules were accordingly placed in positions (*d*), with their centres at $\frac{1}{4}, \frac{1}{4}, \frac{1}{2}$; $\frac{3}{4}, \frac{1}{4}, 0$; $\frac{3}{4}, \frac{3}{4}, \frac{1}{2}$ and $\frac{1}{4}, \frac{3}{4}, 0$.

Fourier transform methods suggested both the orientation of the benzene ring and that the direction of the oxygen–oxygen vector of the quinol molecule should be parallel to *a*. These observations were confirmed by Patterson syntheses calculated for the (010) and (001) projections.

For the acetone molecules, only the positions (*e*) of the *International Tables* $0, y, \frac{1}{4}$; $0, \bar{y}, \frac{3}{4}$; $\frac{1}{2}, y+\frac{1}{2}, \frac{1}{4}$; $\frac{1}{2}, \bar{y}+\frac{1}{2}, \frac{3}{4}$; are consistent with the molecular symmetry. Approximate y co-ordinates for acetone molecules in these special positions were determined by building a scale model of the structure.

Refinement of the structure

From approximate x, y and z co-ordinates obtained with the aid of the trial model, structure factors for $h0l$ and $hk0$ reflexions were calculated. The signs so obtained, together with the observed structure factors led to Fourier electron-density projections on (010) and (001). These were refined in the usual way and the final electron-density maps are shown in Fig. 1(*a*) and (*b*). On these and subsequent maps the positions of the molecules are indicated by full lines and the hydrogen bonds are shown as broken lines. Refinement was continued by calculating difference syntheses for both projections. At first, hydrogen atoms were omitted from F_c and peaks showing their positions gradually became distinguishable on the difference maps as the positions and temperature factors of the heavier atoms were improved. None of the hydrogen atom positions could be determined with certainty from the maps and particular difficulty was experienced in the region of the methyl group of the acetone molecule, because of the overlapping of hydrogen and heavier atoms in both projections. Eventually, however, indications of the positions of the methyl hydrogen atoms were found

Table 1. *Observed and calculated F values*

hkl	F_o	F_c
200	3·8	+ 2·1 a + 2·6 *b*
400	19·0*	+19·0 *a* +20·4 *b*
600	3·3	− 2·4 *a* − 1·8 *b*
800	15·4	−17·1 *a* −14·2 *b*
10,0,0	50·5	+51·1 *a* +47·8 *b*
12,0,0	15·0	+15·7 *a* +14·3 *b*
14,0,0	4·5	+ 5·9 *a* + 3·4 *b*
16,0,0	3·3	+ 4·9 *a* + 5·4 *b*
18,0,0	9·3	+10·0 *a* +10·6 *b*
20,0,0	2·4	+ 1·1 *a* + 2·3 *b*
22,0,0	3·8	+ 3·0 *a* + 3·0 *b*
020	89·1*	−90·7 *c* −90·9 *b*
040	22·6*	+23·4 *c* +25·0 *b*
060	4·5	− 4·3 *c* − 5·4 *b*
080	5·9	+ 5·5 *c* + 6·2 *b*
110	37·1*	−36·9
310	6·5	− 8·6
510	29·2	−31·3
710	30·9	−32·0
910	14·1	−12·3
11,1,0	25·8	−24·2
13,1,0	< 2·9	+ 3·2
15,1,0	7·2	− 7·8
17,1,0	< 3·0	+ 0·1
19,1,0	6·0	− 2·9
21,1,0	4·1	− 2·9
220	6·9	− 7·4
420	49·9*	+49·4
620	29·5	+29·0
820	17·8	+17·9
10,2,0	7·8	− 6·6
12,2,0	7·6	− 6·8
14,2,0	15·2	+12·7
16,2,0	2·5	+ 0·8
18,2,0	6·7	− 4·9
20,2,0	< 2·2	+ 1·7
130	6·0	− 5·4
330	24·0	−25·5
530	10·3	−13·6
730	4·7	+ 3·2
930	4·1	+ 2·8
11,3,0	12·6	+13·8
13,3,0	14·4	−12·6
15,3,0	< 3·1	− 3·1
17,3,0	5·5	− 3·9
19,3,0	< 2·3	+ 0·3
21,3,0	1·8	+ 1·8
240	34·2*	+32·7
440	17·9	−19·9
640	11·3	+10·6
840	6·5	+ 7·3
10,4,0	5·5	+ 6·3
12,4,0	16·5	+16·6
14,4,0	9·3	− 7·8
16,4,0	3·8	+ 3·5
18,4,0	5·6	+ 4·0
20,4,0	< 1·1	+ 0·2
150	11·3	−13·0
350	2·4	− 2·6
550	< 2·9	− 0·9
750	13·6	−13·5
950	16·8	−15·8
11,5,0	8·3	− 8·6
13,5,0	4·5	− 4·8
15,5,0	6·7	+ 6·6
17,5,0	4·8	− 3·4
260	6·9	+ 7·5
460	9·0	+ 9·8
660	< 3·1	− 1·0
860	5·6	+ 5.8
10,6,0	2·9	− 2·5
12,6,0	< 2·7	− 0·7
14,6,0	4·7	+ 5·9
16,6,0	< 1·7	+ 0·6
170	3·1	+ 3·3
370	4·8	− 5·9
570	< 3·0	− 0·5
770	< 2·9	− 0·6
970	4·1	+ 5·3
280	6·0	− 6·9
480	< 2·5	+ 1·0
680	< 2·3	+ 2·4
880	< 2·0	− 1·7
10,8,0	1·8	+ 2·5
190	2·9	− 3·3
390	2·7	+ 2·9
$\bar{2}02$	79·0*	−77·1 *a* −73·8 *c*
$\bar{4}04$	27·6	−29·1 *a* −30·1 *c*
$\bar{6}06$	< 5·5	+ 0·2 *a* + 1·5 *c*
$\bar{8}08$	< 5·0	− 1·7 *a* − 1·8 *c*
$\bar{4}02$	109·3*	−109·1
$\bar{6}02$	68·9*	−69·8
$\bar{8}02$	43·6	−46·2

Table 1 (*cont.*)

hkl	F_o	F_c
$\overline{10},0,2$	30·5*	+33·6
$\overline{12},0,2$	14·2	−11·4
$\overline{14},0,2$	10·8	− 9·8
$\overline{16},0,2$	22·5	−21·8
$\overline{18},0,2$	3·2	+ 1·7
$\overline{20},0,2$	6·9	− 6·6
$\overline{22},0,2$	3·9	− 3·9
002	61·8*	+60·0
202	3·9	+ 1·8
402	49·6*	−49·5
602	20·9	−23·9
802	19·9	−20·9
10,0,2	16·3	−16·7
12,0,2	5·1	+ 6·9
14,0,2	27·6	−27·9
16,0,2	< 5·3	+ 3·5
18,0,2	< 4·1	+ 0·0
20,0,2	< 2·1	− 3·3
004	20·0	+20·1
204	33·3*	+35·8
404	11·5	−10·8
604	21·1	+20·6
804	15·4	+12·8
10,0,4	4·1	+ 3·1
12,0,4	16·3	+13·9
14,0,4	11·2	−10·4
16,0,4	< 3·0	+ 3·1
$\bar{2}04$	31·5*	+31·3
$\bar{6}04$	21·1	+21·4
$\bar{8}04$	30·8	+31·0
$\overline{10},0,4$	31·2	+31·2
$\overline{12},0,4$	34·4	+34·2
$\overline{14},0,4$	14·7	−13·8
$\overline{16},0,4$	< 5·5	+ 0·5
$\overline{18},0,4$	8·3	+ 7·6
$\overline{20},0,4$	3·4	+ 1·3
$\overline{22},0,4$	6·0	+ 5·8
$\bar{2}06$	4·6	− 5·6
$\bar{4}06$	20·9	−22·1
$\bar{8}06$	5·7	− 5·6
$\overline{10},0,6$	6·4	− 6·9
$\overline{12},0,6$	10·8	+11·1
$\overline{14},0,6$	34·4	−33·6
$\overline{16},0,6$	< 5·5	+ 0·5
$\overline{18},0,6$	4·8	− 3·7
$\overline{20},0,6$	< 4·1	− 3·4
$\overline{22},0,6$	5·7	+ 5·6
006	< 5·5	+ 0·1
206	10·8	−11·1
406	14·7	−13·4
606	< 5·3	− 2·4
806	3·9	− 3·8
10,0,6	2·1	+ 3·0
12,0,6	< 3·9	− 1·9
$\bar{2}08$	< 4·8	− 3·0
$\bar{4}08$	7·6	+ 6·3
$\bar{6}08$	5·1	+ 6·0
$\overline{10},0,8$	8·5	+ 8·6
$\overline{12},0,8$	4·6	+ 3·2
$\overline{14},0,8$	4·6	− 3·5
$\overline{16},0,8$	3·9	+ 4·1
$\overline{18},0,8$	5·7	+ 4·5
008	17·0	+17·3
208	5·7	− 6·0
408	< 3·0	+ 0·9
$\bar{1}11$	51·4	−52·6
$\bar{3}13$	45·5	−47·1
$\bar{5}15$	10·5	+ 7·5
$\bar{7}17$	< 3·7	+ 1·3
$\bar{9}19$	5·1	+ 7·0
$\bar{2}22$	3·6	− 2·0
$\bar{4}24$	27·4	+33·9
$\bar{6}26$	3·6	− 3·7
$\bar{8}28$	< 3·1	+ 1·8
$\bar{1}31$	2·0	+ 0·2
$\bar{3}33$	7·9	+ 8·7
$\bar{5}35$	3·6	+ 5·9
$\bar{7}37$	< 3·6	− 2·2
$\bar{9}39$	1·5	− 1·7
$\bar{2}42$	6·0	− 9·0
$\bar{4}44$	3·2	+ 3·0
$\bar{6}46$	3·4	− 3·2
$\bar{8}48$	< 2·4	+ 0·9
$\bar{1}51$	< 3·4	+ 2·0
$\bar{3}53$	3·6	− 5·2
$\bar{5}55$	< 3·7	+ 2·2
$\bar{7}57$	3·6	+ 2·5
$\bar{2}62$	< 3·7	− 0·2
$\bar{4}64$	4·0	+ 3·6
$\bar{6}66$	4·6	− 2·5
$\bar{1}71$	14·0	+14·7
$\bar{3}73$	4·0	− 1·1
$\bar{5}75$	4·8	+ 2·1
$\bar{2}82$	< 2·9	− 1·3
$\bar{4}84$	4·6	− 1·7
$\bar{1}91$	5·2	− 4·0

Where more than one value for F_c is quoted these arise because of the different isotropic temperature factors assumed in the three projections. The projection for which each value was calculated is quoted thus: $a = h0l$, $b = hk0$ and $c = [101]$. F_o values which have been corrected for extinction are denoted by an asterisk.

Table 2. *Co-ordinates, temperature factors, peak electron densities and curvatures for the carbon and oxygen atoms of one asymmetric unit*

Atom	x/a	y/b	z/c	B_{h0l} (Å^2)	B_{hk0} (Å^2)	$\varrho_0 h0l$ (e.Å^{-2})	$\varrho_0 hk0$ (e.Å^{-2})	$C_n h0l$ (e.Å^{-4})	$C_n hk0$ (e.Å^{-4})
C_1	0·175	0·264	0·498	3·25	4·00	8·06	7·10	−114	−108
C_2	0·224	0·133	0·616	3·75	5·00	7·83	6·98	−111	−112
C_3	0·199	0·385	0·382	3·25	5·00	7·83	6·87	−111	−111
C_4	0·064	0·800	0·409	5·60	5·60	8·06	7·03	−62	−65
C_5	0·000	0·702	0·250	4·65	4·65	15·88	6·55	—	−88
O_1	0·000	0·521	0·250	4·65	4·80		—	—	—
O_2	0·101	0·278	0·502	5·00	4·80	10·67	10·52	−98	−97

which were consistent on the two projections, and were also in agreement with the expected bond lengths and angles. In the last stages, all the hydrogen atoms were included in the calculation of structure factors, and this caused an improvement in R of about 0·05 for each projection.

In the later stages of refinement allowances were also made for extinction and for reflexions which were too weak to be observed. The correction for extinction was made according to the method of Pinnock, Taylor & Lipson (1956) by plotting I_c/I_o versus I_c, where I is the intensity not corrected by the Lorentz polarization factor. The method is based on the assumption that secondary extinction reduces the true intensity I to the observed value I_o by the ratio $\mu/(\mu+gI)$, where μ is the linear absorption coefficient and g is a constant. If I is taken as being equal to the calculated value I_c, the following relationship should hold:

$$\frac{I_c}{I_o} = 1 + \frac{g}{\mu} \cdot I_c \,.$$

This was confirmed by the fact that a linear graph was obtained and the graph was used to correct the intensities of the 400, 020, 040, 110, 420, 240, $\bar{2}02$, $\bar{4}02$, $\overline{10}02$, 002, 402 and $\bar{2}04$ reflexions. Reflexions too weak to be observed were accounted for by including a term $(\frac{1}{2}F_{\text{min.}} - F_c)$ in the difference syntheses for every reflexion having $F_c > F_{\text{min.}}$ (where $F_{\text{min.}}$ is the minimum value of F observable at the appropriate value of $\sin\theta$). These terms were also included in the calculation of R. Values of F_o and final values of F_c are shown in

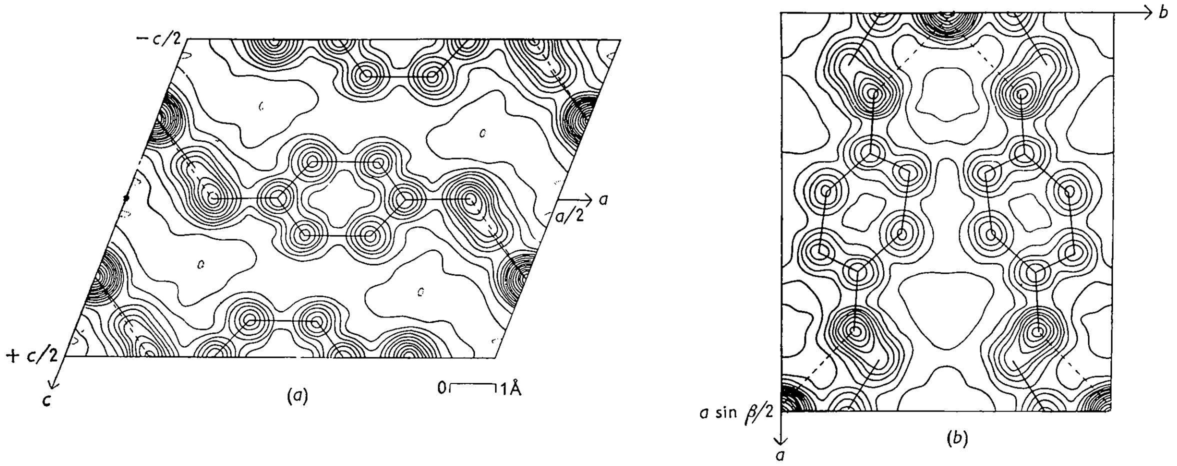

Fig. 1. (*a*) Final Fourier *h*0*l* projection. Contours at intervals of 1 e.Å^{-2}; zero contour dotted. (*b*) Final Fourier *hk*0 projection. Contours as for (*a*), the lowest contour being 1 e.Å^{-2}.

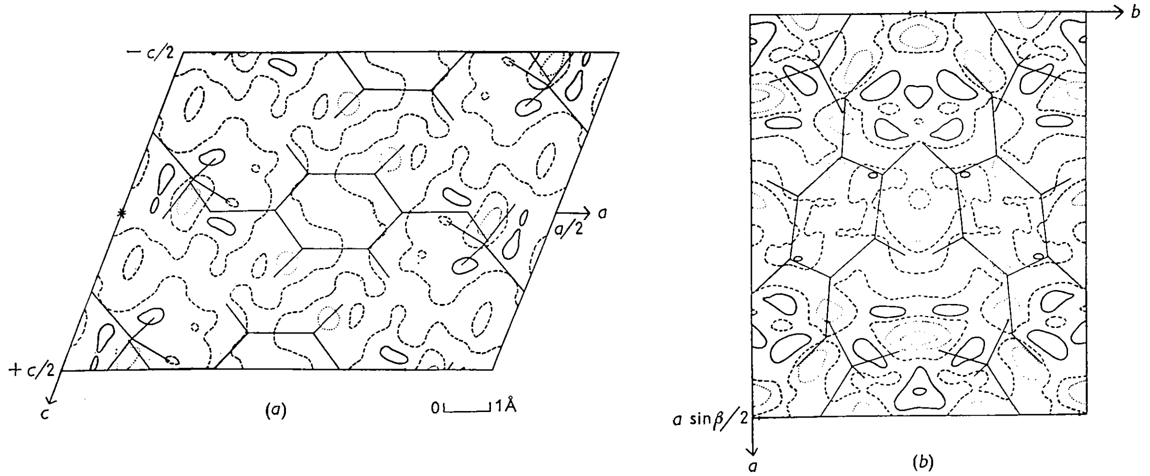

Fig. 2. (*a*) Final difference *h*0*l* projection. (*b*) Final difference *hk*0 projection. Contours at intervals 0·25 e.Å^{-2}. The zero contour is shown as a dotted line and negative contours as broken lines.

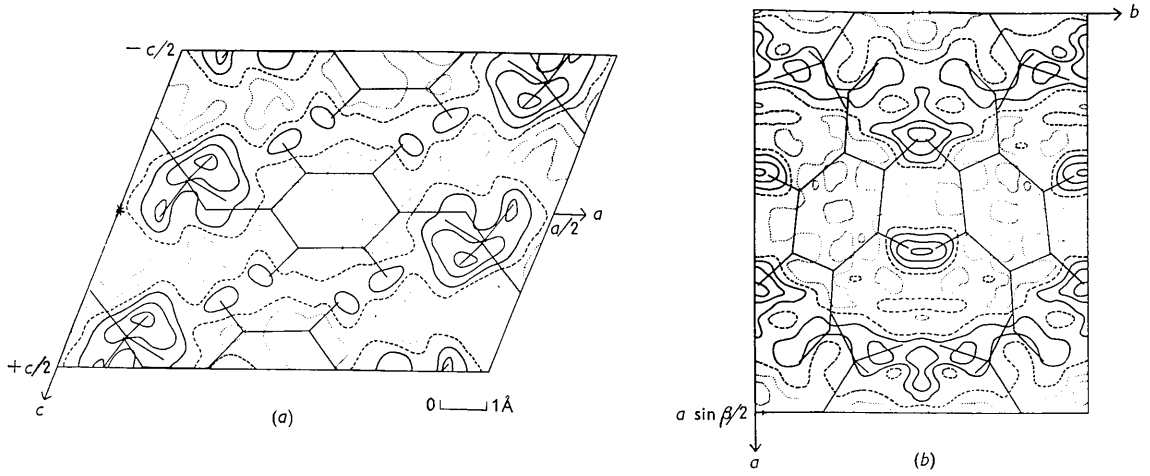

Fig. 3. (*a*) Fourier *h*0*l* and (*b*) Fourier *hk*0 projections with carbon and oxygen atoms removed. Peaks indicate positions of hydrogen atoms. Contours as for Fig. 2.

Table 1. These values of F_c were obtained using the final atomic positions, McWeeny atomic scattering factors (McWeeny, 1951) and the isotropic temperature factors B shown in Table 2. The final value of R for the $h0l$ projection was 0·06 and that for $hk0$ was 0·09.

The final difference maps are shown in Fig. 2(*a*) and (*b*). The standard deviation in electron density calculated by the method of Cruickshank (1949) was 0·148 e.Å^{-2} for the $h0l$ projection, and 0·163 e.Å^{-2} for the $hk0$ projection. The maximum deviation of electron density from zero in the final difference maps is of the order of three standard deviations.

Difference maps calculated on the same basis, but with hydrogen atom contributions omitted from F_c are shown in Fig. 3(*a*) and (*b*). These show the extent to which it is possible to determine the positions of the hydrogen atoms in this structure, and the positions actually assumed are indicated.

The final atomic co-ordinates for the carbon and oxygen atoms of one asymmetric unit are shown in Table 2. The x co-ordinates were obtained from both the $h0l$ and $hk0$ projections and are identical to the accuracy quoted. The different values of B obtained for these two projections are, however, quoted separately. Values of central peak density ϱ_0 and curvature C_n calculated from the final electron-density maps are also quoted separately for the two projections. Resolved peaks are very nearly circular so, for each projection, only one value of curvature is quoted for each atom. Where no value is shown, this is because a satisfactory value is unobtainable due to the overlapping of peaks.

Table 3. *Estimated standard deviations for atomic co-ordinates*

Atom	σ_x (Å)	σ_y (Å)	σ_z (Å)
C_1	0·0039	0·0045	0·0039
C_2	0·0041	0·0043	0·0040
C_3	0·0041	0·0044	0·0040
C_4	0·0072	0·0075	0·0071
C_5	—	0·0055	—
O_1	—	—	—
O_2	0·0046	0·0050	0·0045

The accuracy of atomic positions was calculated from the peak curvatures by the method of Cruickshank (1949) and the standard deviations for the x, y and z co-ordinates so obtained are shown in Table 3. The value reported for σ_x is that determined for the $h0l$ projection. It can be seen that apart from the methyl carbon atom C_4, the standard deviations obtainable are all of the order of 0·004 Å. It may be presumed that the unobtainable values will also be of approximately this magnitude. For all bonds not involving C_4, therefore, the standard deviation of bond length is approximately 0·006 Å, and these bond lengths can be regarded as being accurate to 0·02 Å. Assuming that the σ_y value for C_5 applies equally in any direction, the carbon to methyl bond in acetone has a standard deviation of bond length of approximately 0·009 Å, so this bond can be regarded as being accurate to 0·03 Å.

On the basis of the co-ordinates obtained from the $h0l$ and $hk0$ projections, structure factors were calculated for the projection along the [101] axis, using McWeeny atomic scattering factors modified by an average temperature factor with $B = 4·65$. Refinement of this projection was not possible, due to serious overlapping of all atoms. Comparison of F_o and F_c gave a value of R of 0·11 and the calculated signs together with the values of F_o gave the Fourier electron-density projection shown in Fig. 4.

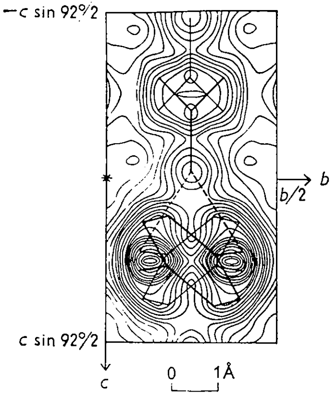

Fig. 4. Fourier projection along the [101] axis. Contours at intervals of 1 e.Å^{-2}, the lowest contour being 1 e.Å^{-2}.

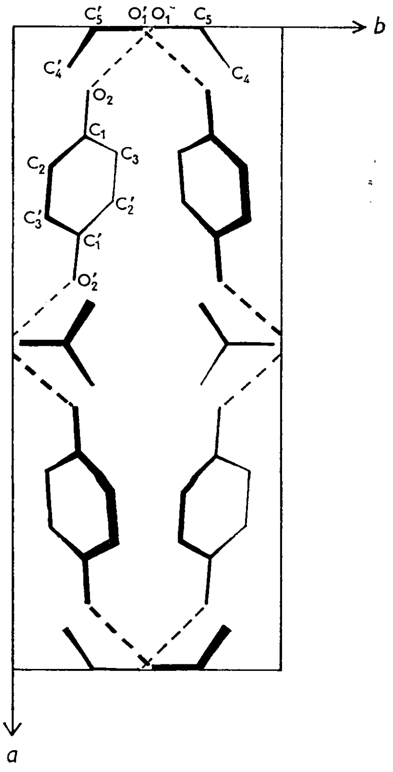

Fig. 5. Contents of one unit cell projected down the *c* axis.

Description of the structure

Fig. 5 shows a view of the structure looking along the *c* axis. It can be seen from this that the structure consists of infinite chains of alternate quinol and acetone molecules joined by hydrogen bonds. In this way each oxygen atom of an acetone molecule receives two hydrogen bonds from the OH groups of quinol molecules on either side of it. Adjacent chains are held together by van der Waals forces between quinol molecules, which have the edge-to-plane packing typical for small aromatic molecules, and between quinol and acetone molecules. The only intermolecular distances other than the hydrogen bonds which are less than 3·5 Å are between each OH group and the C, O and methyl group of an adjacent acetone molecule e.g. between O_2 and atoms C_5', O_1' and C_4' in Fig. 5. These distances are 3·07, 3·46 and 3·37 Å respectively.

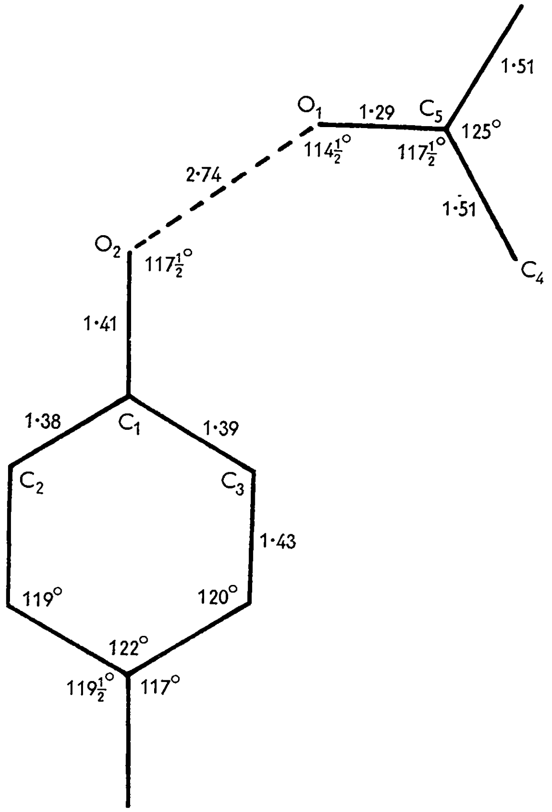

Fig. 6. Lengths (in Å) and angles for covalent and hydrogen bonds.

The lengths and angles for the covalent and hydrogen bonds are shown in Fig. 6. Values for bonds to hydrogen atoms are not shown because the latter could only be located with sufficient accuracy to show that their positions were consistent with expected dimensions.

Discussion

The structure determination has established that the complex is a hydrogen bonded molecular compound rather than a clathrate or a channel structure.

The formation of this type of complex is apparently specific to acetone, and attempts to form similar complexes with a wide variety of aldehydes and ketones have been unsuccessful. A plausible explanation of this appears if the structure is considered as being composed of alternate layers of quinol and acetone molecules parallel to (100). Within each quinol layer the edge-to-plane packing will determine the approximate dimensions for the *bc* cross-section of the unit cell. The acetone molecules then perform the function of joining the quinol layers adjacent to them by accepting two hydrogen bonds at each carbonyl oxygen atom. This will determine the approximate extension of the structure in the *a* direction. If the acetone molecules were replaced by larger ketone molecules, the quinol layers would be forced so far apart that hydrogen bonding would be precluded, whilst with smaller molecules it is possible that there is no way of retaining the structure and using the space efficiently.

It is interesting to compare the dimensions of the acetone molecule found in the present work with those determined by Kimura & Kurita (1951), Allen, Bowen, Sutton & Bastiansen (1952) and Romers & Creutzberg (1956) by the method of electron diffraction. The values reported by these authors are respectively:

$$\begin{aligned} C{-}C &= 1{\cdot}55\pm0{\cdot}03,\ 1{\cdot}55\pm0{\cdot}02,\ 1{\cdot}52_5\ \text{Å};\\ C{=}O &= 1{\cdot}24\pm0{\cdot}03,\ 1{\cdot}22\pm0{\cdot}03,\ 1{\cdot}24\ \text{Å};\\ \angle C{-}C{-}O &= 121{\cdot}5\ \pm2^\circ,\quad 119{\cdot}6\pm3^\circ,\ 118{\cdot}5^\circ. \end{aligned}$$

The differences between these values and those recorded in Fig. 6 are probably significant, even when allowance is made for experimental errors in the separate determinations. These differences may be due to the fact that the acetone molecule in the complex is hydrogen bonded, since they would be consistent with an increased contribution to the resonance state of the molecule by the ionic form in which the oxygen atom is negatively charged and the methyl groups are positively charged.

Dimensions for the quinol molecule have been published previously by Palin & Powell (1947). These authors reported that the aromatic ring was a regular hexagon of side 1·39 Å to within 0·03 Å, and that the C–O bond was of length 1·36±0·03 Å. The dimensions found in the present work differ slightly from these values and suggest that the aromatic ring is not quite regular. The distance 1·43 Å between C_3 and C_2' differs from the mean ring C–C distance of 1·40 Å by more than three standard deviations. The C–O distance of 1·41 Å differs significantly from the value of 1·36 Å found not only in quinol, as mentioned above, but also in certain other compounds in which oxygen is attached to an aromatic nucleus. It approaches more closely the generally accepted single C–O distance of 1·42 to 1·44 Å.

It might be expected that the methyl groups would be capable of free rotation in acetone. However, in this complex, the hydrogen atoms attached to the methyl groups of acetone were found to be in fixed positions, which are approximately those expected from the point of view of minimising the interaction of the hydrogen atoms of each methyl group with the oxygen atom and the other methyl group in the molecule. A similar result of fixation of hydrogen atoms in methyl groups has been reported by Goodwin, Przybylska & Robertson (1950) in 1:4 dimethoxybenzene.

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An X-ray Investigation of Lysozyme Iodide and Nitrate

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Cell dimensions and space groups have been determined for the isomorphous lysozyme nitrate and iodide in both wet and dry forms. All are monoclinic $P2_1$, the dry forms showing a halving of the wet cell along the c axis. The molecular weight of lysozyme is 13,900±300 and the iodide has 19 anions per protein molecule. This number of iodine atoms is too great to permit the use of the isomorphous-replacement method of structure determination.

Introduction

Lysozyme is a readily available globular protein of low molecular weight and as such should be suitable for exhaustive X-ray analysis. It has the added advantage that it is a very basic protein which forms crystalline salts with mineral acids. The chloride, which crystallizes in the tetragonal system, has been studied by Palmer, Ballantyne & Galvin (1948) and by Corey, Donohue, Trueblood & Palmer (1952). Carlisle (1949) has examined the bromide. Crick's (1953) examination of the iodide and nitrate showed them to be isomorphous with the bromide. The present work is concerned with the possibility of using the method of isomorphous replacement to study the structure of lysozyme by comparison of the iodide and the nitrate.

Preparation of the crystals

The salts were prepared from isoelectric chick lysozyme supplied by Armour & Co. Ltd., following the method of Alderton & Fevold (1946). Although the iodide crystallized easily in a few days, it was found desirable to use a 0·5% protein solution instead of the recommended 2%. In order to obtain single crystals of the nitrate, it was necessary to reduce the potassium nitrate concentration from 5% to 2·5%, when reasonable crystals were obtained after a few weeks.

Wet crystals were preserved by mounting in sealed Pyrex capillary tubes together with a little mother liquor. Dry crystals were prepared by removing adhering liquid with filter paper and immersing the crystals in xylene which was then allowed to evaporate. Xylene-dried protein crystals have been found to give better X-ray diffraction patterns than air-dried crystals (Low & Richards, 1954).

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