118. *The Structure of Molecular Compounds. Part V. The Clathrate Compound of Quinol and Methanol.*

By D. E. Palin and H. M. Powell.

The substance formerly described as β-quinol is shown by chemical analysis, by molecular-weight determination from unit cell dimensions, and by detailed crystal structure determination to be a compound $3C_6H_4(OH)_2,CH_3{\cdot}OH$. The structure, similar to that of the corresponding compound of quinol with sulphur dioxide, consists of two interpenetrating giant molecules of hydrogen-bonded quinol units. The methanol molecules are imprisoned in cavities between the two giant molecules. They are arranged with their long axes parallel to the *c* direction of the hexagonal axes and the structure is thus non-centrosymmetric.

On crystallisation from water, ethanol, or ether, quinol forms needle-like hexagonal crystals, but when methanol is used as solvent stout hexagonal prisms with rhombohedron terminations are obtained. The crystals formed in these two cases are morphologically different although it is not clear whether this was observed by early crystallographers. Groth (*Ber.*, 1868, **1**, 164) stressed the needle character of the crystals obtained from water, but the interfacial angles that he gives are similar to those of Heydrich (*Z. Krist.*, 1911, **48**, 260), who carried out his measurements on crystals grown from methanol and are in agreement with those reported below. The two forms obtained from water and methanol were, however, clearly distinguished by Caspari (*J.*, 1926, 2944; 1927, 1093), who called them α- and β-quinol respectively. He gave for α-quinol the unit cell dimensions $c = 5{\cdot}62$, $a = 22{\cdot}08$ A., space-group C_{3i}^1 with 18 molecules per unit cell. For β-quinol he found $c = 5{\cdot}53$, $a = 16{\cdot}25$ A. with 9 molecules per unit cell. He found dissimilar terminal faces $\{10\bar{1}1\}$ and $\{20\bar{2}\bar{3}\}$ for the ends of the crystals and gave the space-group as C_3^1.

During the early stages of the crystal-structure analysis of the compound 3 quinol : SO_2 (Part III, *J.*, 1947, 208) it was noted that in cell dimensions, certain morphological characteristics, and general pattern of *X*-ray diffraction effects there was a strong similarity between this compound and " β-quinol " as described by Caspari, and *X*-ray photographs were made of both with a view to their possible use for deducing signs of the structure factors from the differences in the two sets of intensities. For " β-quinol " the space-group found was $R3 - C_3^4$, not C_3^1 as proposed by Caspari. Moreover, the observed *a* dimension, $16{\cdot}5_6$ *kX*, differed appreciably from that given by Caspari, and consequently the weight of the unit cell was greater than that corresponding to 9 molecules of quinol. In view of this complication and a confirmation by a positive pyroelectric test of the hemimorphism reported by Caspari (which is not found for the sulphur dioxide compound), the structure given in Part III was obtained by other methods. From the results of this determination and an examination of other similar compounds (to be described in Part VI) it seemed clear that all the compounds in this series had a similar structure of two interpenetrating giant molecules of hydrogen-bonded quinol enclosing the sulphur dioxide or other molecule. It seemed impossible to account for the non-centrosymmetric character of the crystals obtained from methanol if they consisted of the quinol structure only. The observed structure-factor values also were such that it appeared certain that they must give a noticeable electron density in the region corresponding to the sulphur dioxide or other molecule. These observations, combined with the knowledge of the excess weight of the unit cell, led to the view that the crystals were not those of a modification of pure quinol but that they contained a second component. The most likely added molecule was methanol, although there was a possibility that water might also be present if the solvent used was not anhydrous.

It was next proved that the compound could be obtained from pure anhydrous methanol, and confirmation of the presence of methanol in the crystalline compound was obtained by dissolving a quantity of it in water and distilling in an all-glass apparatus. Distillation started at 99° and the distillate, which smelt of methanol, had a specific gravity less than 1·00. There may have been some distillation in steam of quinol, and an accurate estimate from the specific gravity of the concentration of methanol in the original material could not be expected. Analyses showed the composition of the *compound* to be approximately 3 quinol : MeOH.

Since the quinol part of the structure is evidently very nearly the same as that in the centrosymmetric sulphur dioxide compound, the non-centrosymmetric character must arise from the methanol molecules. It seemed likely therefore that these molecules were oriented with their lengths parallel to the *c* axis, and from a consideration of the state of the sulphur dioxide molecule in the corresponding structure it seemed probable that the methanol molecule would be free to undergo considerable motion in the neighbourhood of the axis. If this general arrangement is correct, it is readily seen that, although the structure as a whole is polar and conforms to the space-group $R3$, a projection of the structure on the c face would be centrosymmetric and the corresponding Fourier summation of electron density could be carried out by use of the experimental F_{hki0} values with a positive or negative sign as required.

In the ideal case, where the only difference between two structures lies in the electron weight of the scattering unit at a symmetry centre, any changes in reflexion intensity must be due to change in positive contribution of this unit as, *e.g.*, in the phthalocyanines (Robertson, *J.*, 1935, 615; 1936, 1195; Robertson and Woodward, *J.*, 1937, 219). The signs of the stronger reflexions or of those which are absent in one case or the other may be determined unequivocally, but for the weaker reflexions it is difficult to be certain whether or not a sign reversal has occurred. In the present case, however, the position is further complicated by the small changes in atomic parameters for the quinol molecules to be expected in consequence of the differences in cell dimensions, and by the fact that the scattering unit at the origin can only be considered to be distributed about this point in some way. Since, however, the signs for the F_{hki0} terms in the sulphur dioxide compound had already been computed, it was possible to allot signs to the methanol compound terms as follows. The structure-factor values for the two compounds, reduced to a similar scale, were tabulated together with the signs previously derived for the sulphur dioxide compound. Signs for the methanol compound were allotted on the assumption that the changes in magnitude are due to the decrease in positive contribution of the scatterer at the origin in the methanol compound and that they are influenced to only a minor extent by changes in the quinol co-ordinates. These results are shown in Table I. In general, structure factors which are positive for the sulphur dioxide compound are decreased in magnitude for the methanol compound, and for negative structure factors the converse is true. In the same way, except for $F_{16\,1\,\overline{17}\,0}$, spectra which are absent in the methanol compound have weak positive values in the sulphur dioxide compound, and this justifies the allocation of negative signs to those which were observed for the methanol compound but not for the sulphur dioxide compound. The structure factors which do not comply with the above generalisations are indicated in the table. Except for $F_{7\,4\,\overline{11}\,0}$ there appears to be little doubt about the correctness of the sign given, on account of the decisive nature of the calculated sign for the sulphur dioxide compound. For $F_{7\,4\,\overline{11}\,0}$ an increase in magnitude for the methanol compound was observed and since the calculated positive value for the sulphur dioxide was not sufficiently high to be conclusive, it was decided to take the sign as a negative in the methanol compound. It will be seen that the maximum number of negative signs has been allotted, so that any electron density shown at the origin in the projection provides certain proof of the presence of scattering matter near this point.

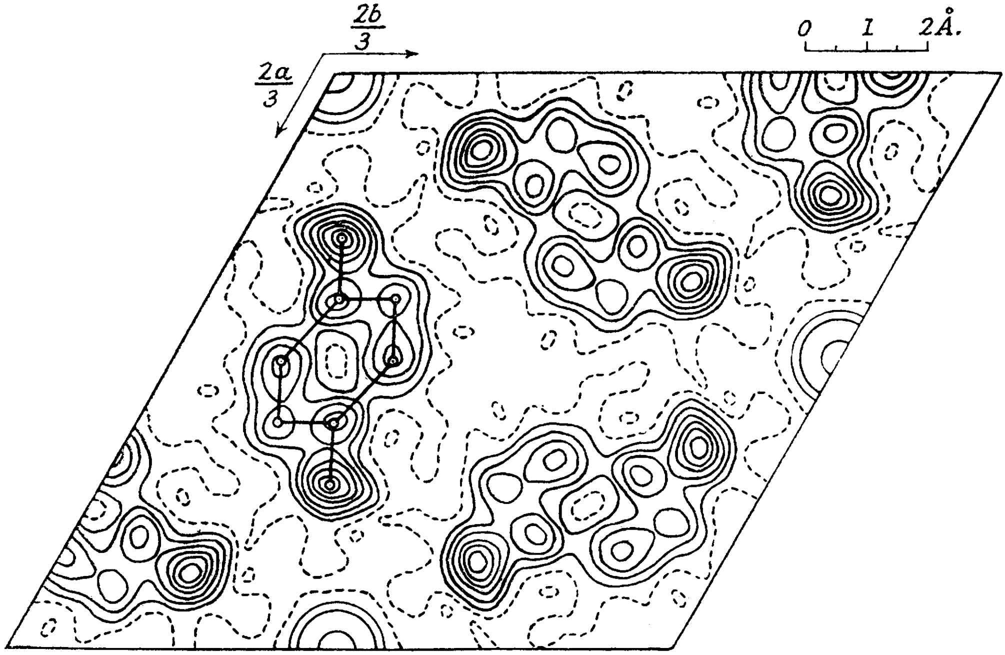
TABLE I.

Allocation of signs for F_{hki0}.

Indices	SO_2 compound.		MeOH compound.		Indices	SO_2 compound.		MeOH compound.	
hk.	F.	Sign.	F.	Sign deduced.	*hk*.	F.	Sign.	F.	Sign deduced.
0 3	44	—	66	—	5 2	58	+	45	+
0 6	28	—	45	—	5 5	8	+	*a*	*a*
0 9	48	+	42	+	7 1	21	+	*a*	*a*
0 15	9	+	13	+ *	7 4	12	+	23	— *
1 1	28	—	15	— *	7 7	39	+	42	+
1 4	70	+	46	+	7 10	17	—	15	— *
1 7	13	—	23	—	8 2	27	—	36	—
1 13	17	—	18	—	8 11	13	+	12	+
2 2	86	+	69	+	9 9	*a*	*a*	11	—
2 5	57	+	48	+	10 1	37	+	35	+
2 8	22	—	29	—	10 4	17	—	15	— *
2 11	10	+	15	+ *	10 7	21	—	15	— *
3 3	90	+	76	+	11 2	17	+	18	+
3 6	23	+	14	+	11 8	*a*	*a*	12	—
3 9	14	+	15	+	12 3	14	—	18	—
3 12	17	—	15	—	13 1	22	—	18	—
4 1	35	—	46	—	13 4	15	+	13	+
4 4	34	+	26	+	16 1	11	—	*a*	*a*
4 13	*a* †	*a* †	12	—					

* The structure factors marked * do not conform to the generalisations mentioned in the text.
† *a* denotes "absent."

The electron-density plot is shown in the figure. It is very similar in general appearance to the corresponding projection for the sulphur dioxide compound (Fig. 6, Part III, *loc. cit.*), but with a much reduced peak at the origin. The oxygen atoms of the quinol molecules are seen grouped in hydrogen-bonded hexagons around the symmetry axes. The side of the hexagon is $2{\cdot}7_1$ A. with little change from that in the sulphur dioxide compound, but since the projected length oxygen–oxygen in the same quinol molecule has increased from $3{\cdot}9_5$ to $4{\cdot}1_2$ A. there must be a corresponding decrease in the angle of tilt of this oxygen–oxygen axis to the plane of the projection. The angle, 45° in the sulphur dioxide compound, decreases to about 41½°. This change of tilt, which is related to the alterations in cell dimensions, is discussed further in Part VI in relation to other structures in this same series. It was assumed that the quinol molecule would have the same shape and dimensions as determined in Part III, and on the basis of this and the electron-density projection the atomic parameters of Table II were estimated.



Relative electron density projected on (0001). *The atomic centres are indicated for one quinol molecule.*

Table II.

Atom.	x.	y.	Atom.	x.	y.
Quinol oxygen	$0{\cdot}19_0$	$0{\cdot}10_0$	Carbon C_2	$0{\cdot}33_0$	$0{\cdot}11_0$
Carbon C_1	$0{\cdot}26_1$	$0{\cdot}13_1$	,, C_3	$0{\cdot}26_1$	$0{\cdot}18_9$

From the good resolution, compatibility with required molecular dimensions, and absence of unwanted peaks in the projection it seems unlikely that there can be serious errors in the F_{hki0} terms or their signs, and it is therefore necessary to consider the heights of the various peaks. For the oxygen atom and carbon atoms C_1,C_2,C_3 these heights in arbitrary units above an estimated zero are 38, 29, 26, and 23. With allowance for the hydrogen atoms associated with each atom the corresponding electron weights, commonly observed to give a rough parallelism with these heights, are 9, 6, 7, 7. The oxygen and C_1 peaks are in about the expected ratio, but C_2 and C_3 are distinctly lower than C_1 whereas they might be expected to be higher. The peaks are affected in different ways by their neighbours but the effect seems to be real: it was also noticed for the sulphur dioxide compound in the projection which is derived from an independent set of observed F_{hk0} magnitudes. It may be explained by the oscillation of the quinol molecule about its oxygen–oxygen axis. This leaves the atomic centres of the C_1 atoms and of the oxygen, which is fairly firmly held at both ends through hydrogen bonds, in their original positions but displaces the centres of C_2 and C_3 with a consequent broadening and lowering of the electron-density peaks.

The peak at the origin has a height of 21 (on the same arbitrary scale), slightly less than that of C_3 and much smaller than would be expected for a methanol molecule if it were fixed with its carbon–oxygen line on the *c* axis. It is also a rather flat peak, and it seems probable that these effects arise from considerable movement of the methanol molecule in its enclosing cavity, when the electron density that should correspond to it tends to become lost in the surrounding background. That there could be such motion is known from the nature of the enclosure and from observations on the sulphur dioxide in its similar cavity. It provides further evidence that the relationship of the two molecular species in these molecular compounds is that of enclosure of one in a cagework of the other rather than that of any union by chemical bonds.

EXPERIMENTAL.

Crystals were obtained by slow crystallisation from a saturated solution of quinol in methanol at ordinary temperatures. They were in the form of hexagonal prisms with rhombohedral terminations which in most crystals were the same at both ends although some crystals appeared to be hemimorphic. They were fairly hard, showed no marked cleavage, and had weak negative birefringence. The density (flotation) was $1{\cdot}35_{0\pm5}$. Tests for pyroelectricity by the liquid-air method gave a weak positive result. Morphological data obtained by Miss M. W. Porter, Mineralogy Department, Oxford, on crystals which showed $\{10\bar{1}\}$, $\{100\}$ and $\{11\bar{1}\}$ (rhombohedral indices) are compared with previously reported values :

	Heydrich (*loc. cit.*).	Groth (*loc. cit.*).	M. W. Porter.
$(100) : (10\bar{1})$	58° 4′	58° 22′	58° 13′
$c : a$	0·668	—	0·664

The axial ratio here given corresponds to $2c : a$ for the unit cell derived from *X*-ray examination.

Oscillation and Weissenberg photographs with copper radiation were taken about the same axes as for the sulphur dioxide compound, and structure-factor values derived in a similar manner. The cell dimensions found were $a = 16{\cdot}5_{6\pm3}$, $c = 5{\cdot}5_{5\pm2}$ *kX*. The *c* dimension agrees with that given by Caspari (*loc. cit.*) but that for *a* differs appreciably from his (16·25). The present values give $2c : a = 0{\cdot}671$, more nearly in agreement with the value deduced from crystal measurement.

From the cell dimensions and density the calculated weight of the cell, in molecular weight units, is 1078. This value is 88 in excess of that required for nine molecules of quinol (990). The excess is well outside the experimental error and is compatible with that required for 3MeOH (96).

Analysis of two samples, by F. P. Johnson, I.C.I. Widnes laboratory, gave : C, 63·4, 63·5; H, 5·95, 6·1; $H_2O < 0{\cdot}5$. [$3C_6H_4(OH)_2,CH_3{\cdot}OH$ requires C, 63·0; H, 6·07%. Calc. for quinol: C, 65·4; H, 5·45%]. A separate determination of the methanol content was also made. The methanol was separated from quinol by azeotropic distillation with water, and isothermally distilled from this distillate into excess of acid dichromate; back titration of the excess of dichromate gave: MeOH, 8·6 [$3C_6H_4(OH)_2,CH_3{\cdot}OH$ requires $CH_3{\cdot}OH$, 8·85%].

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