163. *The Structure of Molecular Compounds. Part VI. The β-Type Clathrate Compounds of Quinol.*

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

Crystalline compounds of ideal formula 3 quinol : M are shown to have a common structural component consisting of quinol units hydrogen bonded to form two independent interpenetrating giant molecules which together enclose small molecules M of the second component. *X*-Ray and other data are recorded for the compounds where M is SO_2, MeOH, HCl, HBr, H_2S, C_2H_2, $H{\cdot}CO_2H$, CO_2, MeCN. Mixed compounds have also been prepared with two different kinds of molecule in the enclosures. Analyses and molecular-weight determinations from unit-cell dimensions and densities are in agreement in showing that there may be considerable departure from the ideal formula through many of the cavities available for M being unoccupied.

For several compounds in which M is a sufficiently small molecule the dimensions of the quinol structure are almost constant and are determined by the equilibrium of the two interpenetrating giant molecules. The larger enclosed molecules produce minor alterations in the unit-cell dimensions, distending the quinol framework along the *c* direction of the hexagonal cell and contracting it simultaneously at right angles by an effect analogous to the extension of a piece of trellis without alteration in the dimensions of its component parts. These variations have been correlated with the dimensions of the enclosed molecules. Slight alterations in the shape of the quinol cagework, without alteration in the dimensions of the quinol units or their connecting hydrogen-bonded hexagons of OH groups, are made so that the cavities may accommodate the different molecules M. These structural changes have been correlated with the variations in the weak birefringence in the series.

In Part IV (Powell, this vol., p. 61), the conditions of formation and some properties of clathrate compounds formed by enclosure of one kind of molecule by others are discussed. The crystal structures given in detail in Parts III and V (Palin and Powell, *J.*, 1947, 209; this vol., p. 571) show that two interpenetrating giant molecules of hydrogen-bonded quinol units may together enclose molecules M in this way to give complexes formulated as shown, and that there is some freedom of movement of the enclosed molecule which, although firmly retained, need not be closely bound to its surroundings. The present communication contains the results of structural examinations made on some other members of this series of compounds in order to determine whether there is a constant structural type and to find the effects of varying the type and concentration of the enclosed molecule. Some of these compounds have been prepared previously (for references, see Part III) and it is now found that molecules of varied type may be enclosed in this way provided that they satisfy certain size requirements, and do not react chemically with quinol in the conditions of preparation. It is also normally necessary that the added component should exist in the form of molecules in solution with quinol in sufficient concentration to ensure its being trapped during the building up of the structure, although other methods of preparation may sometimes be possible. Some materials containing two kinds of enclosed molecule were also examined.

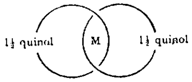


Table I.

M.	Morphology, forms in rhombohedral indices.	Refractive indices, n_D : ω.	Refractive indices, n_D : ε.	Double refrn.	Axial ratio : from interfacial angle.	Axial ratio : 2*c*/*a* from *X*-ray examntn.
SO_2	Yellow hexagonal prisms (10$\bar{1}$) with (100)	$1\cdot62_9$	$1\cdot65_5$	$+0\cdot02_6$	0·714	0·714
SO_2 (specimen *B*)	As above but poorly formed	—	—	—	—	0·680
MeOH	Colourless prisms (10$\bar{1}$) with (100) and (11$\bar{1}$)	$1\cdot63_0$	$1\cdot62_4$	$-0\cdot00_6$	$0\cdot66_4$	$0\cdot67_1$
MeCN	Colourless prisms (10$\bar{1}$) with (100), (1$\bar{1}$0), and (211)	$1\cdot60_6$	$1\cdot66_6$	$+0\cdot06_0$	$0\cdot78_3$	$0\cdot78_0$
$H{\cdot}CO_2H$	Colourless prisms (10$\bar{1}$) with (100) and (21$\bar{1}$)	$1\cdot61_3$	$1\cdot63_3$	$+0\cdot02_0$	$0\cdot68_8$	$0\cdot68_9$
CO_2	Colourless	—	—	—	—	$0\cdot72_0$
HCl	Colourless	$1\cdot63_2$	$1\cdot62_3$	$-0\cdot00_9$	—	$0\cdot66_0$
HBr	Brown	—	—	—	—	$0\cdot66_2$
H_2S	Colourless	$1\cdot65_1$	$1\cdot63_5$	$-0\cdot01_6$	—	$0\cdot66_8$
C_2H_2	Colourless	$1\cdot63_2$	$1\cdot61_2$	$-0\cdot02_0$	—	$0\cdot65_7$
SO_2 + MeOH	Similar to SO_2 above	—	—	—	—	$0\cdot70_1$
SO_2 + HCl	Pale yellow hexagonal prisms	$1\cdot63_0$	$1\cdot62_9$	$-0\cdot00_1$	—	$0\cdot67_3$

All the substances were obtained in stable crystalline forms; some of their properties are summarised in Table I, M representing the enclosed molecule. All except one of these materials melted at about 170° but this temperature probably does not correspond to the melting point of the unchanged substance since it is found that decomposition, with volatilisation of quinol, may occur at temperatures much lower than this. The formic acid compound differed from the others in melting at about 160°. Tests for pyroelectricity by the liquid-air method gave a positive result for the methanol compound, a weak, rather doubtful effect with the methyl cyanide compound and with the mixed compound containing methanol and sulphur dioxide, and no detectable effect with the others.

Very similar *X*-ray diffraction patterns were obtained with all these crystalline materials. The unit-cell dimensions and densities were used to find a unit-cell weight and hence a composition which is compared with that obtained by chemical analysis. The results are collected in Table II in which Q in cols. 6 and 7 represents quinol and the last four columns show the agreement between the compositions derived in the two different ways.

TABLE II.

Added molecule M.		Cell dimension, *kX* U.			Ideal formula 3Q,M.		From *X*-ray results :			From chemical analysis :	
M.	Mol. wt. of M.	*a*.	*c*.	*d*.*	Formula wt. for 3(3Q,M).	M, %.	Mol. wt. per unit cell, obs.	M, %.	Mol. ratio M/3Q.	M, %.	Mol. ratio M/3Q.
HCl	36·5	16·55	5·46	1·38	1100	9·97	1083	8·6	0·85	8·58	0·85
HBr	81	16·57	5·48	1·36	1233	19·7	1075	7·9	0·35	8·1	0·36
H_2S	34	16·58	5·49	1·34	1194	9·35	1060	$6{\cdot}5_5$	0·69	6·2	0·64
C_2H_2	26	16·63	5·46	1·31	1068	7·31	1038	4·6	0·62	—	—
MeOH	32	16·56	5·55	1·35	1086	8·85	1078	8·1	0·92	8·6	0·97
$H{\cdot}CO_2H$	46	16·42	5·65	1·37	1128	12·23	1096	9·7	0·79	10·2	0·82
SO_2	64	16·29	5·81	1·44	1182	16·25	1165	14·8	0·91	14·5	0·88
CO_2	44	16·17	5·82	1·36	1122	11·77	1087	8·9	0·74	8·9	0·74
MeCN	41	15·95	6·24	1·33	1113	11·06	1108	10·7	0·96	11·0	0·99
SO_2 (*B*)	—	16·49	5·60	1·32	1182	16·25	1056	6·2	0·34	*ca.* 5 †	—
SO_2 + MeOH	—	16·35	5·73	1·40	—	—	1125	—	—	—	—
SO_2 + HCl	—	16·47	5·54	$1{\cdot}39_5$	—	—	1100	—	—	3·86 5·78	0·22 0·58

* *d* = Density. † Sample not homogeneous.

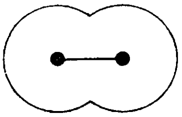
From these results and the close similarity of all the photographs to the corresponding ones obtained for the two compounds which have been examined in detail it is concluded that all these compounds have the same essential structure, with the component M occupying closed cavities in the quinol structure. Two effects may be seen immediately from Table II, *viz.*, that the cavities need not all be occupied, and the cage structure itself may be slightly modified by the enclosed molecule. Although there is one cavity to every three quinol molecules of the cage structure, the number of molecules found to be associated with this amount of quinol may be considerably less than one, *e.g.*, 0·36 in the hydrogen bromide compound, but may approach the ideal value, *e.g.*, 0·99 for methyl cyanide and 0·97 for methanol, and never exceeds it. The cell dimensions, and thus those of the cage structure, are seen to vary slightly from one compound to another.

Although the ordinary α-form of crystalline quinol has a different structure, it appears from experiments reported in Part IV and from further uncompleted work that in special conditions quinol may crystallise in the same form of two interpenetrating quinol frameworks with vacant cavities. This structure is now given the name β-quinol, which should no longer be used to describe the methanol compound. The compounds which contain this as a component are accordingly described as of the β-type. Since this β-structure can exist by itself, it is readily understood how similar structures containing any proportion of M from 0 to 1 molecule for every three quinol molecules may be formed. That the same composition is not always obtained for the same M is shown by the two samples of the sulphur dioxide compound which have 0·91 and 0·34 molecules severally, and by the hydrogen bromide complex reported by Gomberg and Cone (*Annalen*, 1910, **376**, 238) with 15—17% HBr.

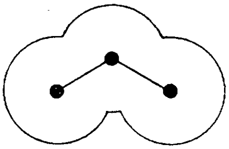
Since the empty β-structure is not readily formed when the solvent or other molecules cannot be enclosed, it seems clear that the enclosure itself exerts a stabilising influence. From solvents with molecules too large or too small for enclosure the much more complex α-structure is formed by an arrangement of quinol molecules such as that suggested in Part IV.

This produces a denser packing although it loses in part the natural way of linking quinol molecules in accordance with the directional requirements of the hydrogen bonds. The calculated density 1·26 for the empty β-structure, considerably lower than the observed value 1·33 for α-quinol, is in agreement with this.

The slight variations in the unit-cell dimensions for the different compounds are related to the dimensions of the enclosed molecule. The atoms of the surrounding cage structure have their centres distributed over the surface of a sphere of diameter slightly less than 8 A., so that an effectively spherical molecule of contact radius 2 A. or more could be contained without undue close approach to any atom of its surroundings. For the molecules HCl, HBr, H_2S, which may be regarded as of this kind, the dimensions of the three unit cells are nearly equal, with the maximum *a* and minimum *c* values found. The other molecules may be regarded for packing purposes as of roughly dumb-bell shape and, owing to the distribution of the surrounding atoms on the sphere with a comparatively wide separation of the hydroxyl groups in their hydrogen-bonded hexagons at the top and the bottom of the cell, the dumb-bell axis must be placed vertically parallel to the *c* axis of the crystal in order to avoid close contacts with the carbon atoms of the quinol molecules. Increase in length of the molecule causes an increase in the *c* dimension. Of the two molecules which may be represented for packing purposes as (I), acetylene produces no increase and the somewhat larger methyl alcohol gives the smallest increase. The similar sulphur dioxide and formic acid molecules represented by (II) give a larger change, about the same as that for carbon dioxide (III), and the greatest increase is found with the linear methyl cyanide molecule which has the greatest length between centres of its terminal atoms. The distensions of the cell along the *c* direction are therefore made to accommodate these lengths, and since the unit cells for the four smallest enclosed molecules have nearly the same dimensions of mean value $a = 16{\cdot}58$, $c = 5{\cdot}47$ *kX* it appears that these represent the natural dimensions determined by the equilibrium of the parts of the quinol frameworks alone. If this is so, the same unit-cell dimensions may be expected for the unfilled β-structure.



(I.)



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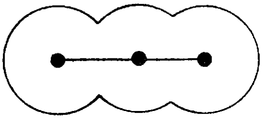
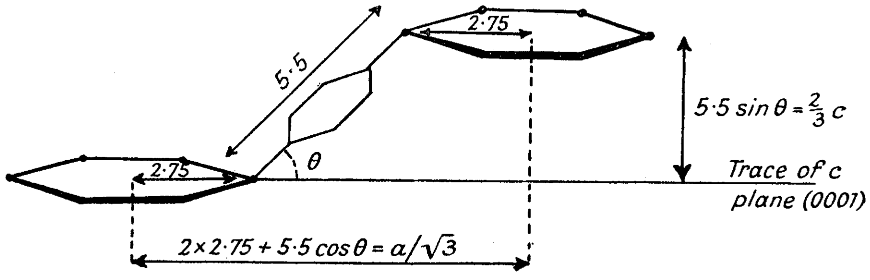


(III.)

Fig. 1.



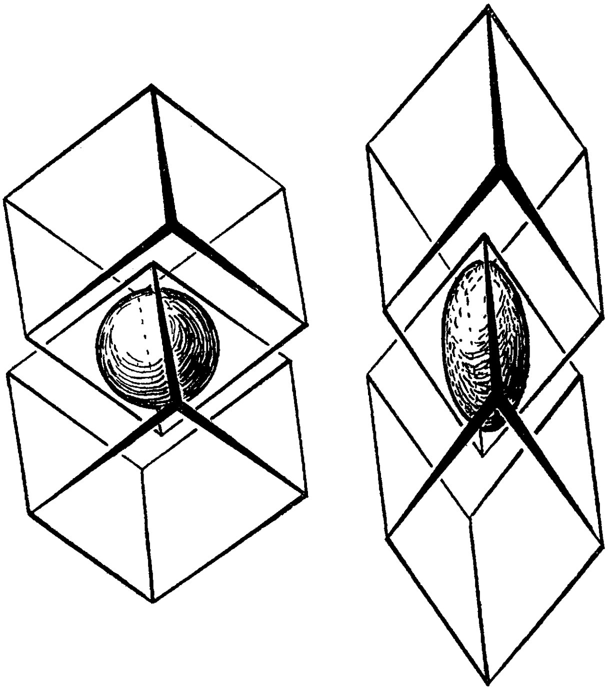
One quinol molecule is shown with its oxygen–oxygen axis inclined at an angle θ to the 0001 *plane. The two hexagons of hydrogen-bonded* OH *groups through which this molecule is linked to the rest of the structure are drawn in, and the way in which the angle θ may be related to either the* a *or the* c *dimension of the unit cell is indicated. Distances marked are in Angström units. The hinging effect is obtained by variation in the angle θ.*

Simultaneously with increase in *c* there is in nearly every case a decrease in the *a* dimension and, if the compounds containing acetylene and those containing two kinds of enclosed molecules are excluded, the order of increasing *c* is exactly the same as that of decreasing *a*. These changes may therefore be explained to a first approximation on the assumption that in all the structures the quinol molecules remain linked through similar hydrogen-bonded hexagons of OH groups and that the quinol molecule as a whole may be regarded as hinged as shown in Fig. 1 at its points of attachment through its oxygen atoms.

Applied to the structure as a whole, this hinging produces an effect of simultaneous extension in height with decrease in cross-section analogous to the changes in overall dimensions of a piece of trellis work produced by varying the angle between its crossed component parts without altering their dimensions. The general character of the effect may be seen from Fig. 2.

On the assumptions that the oxygen–oxygen distance in the quinol molecule is constant (5·5 A.) and that similar plane hexagons of side 2·75 A. join the OH groups in all the structures, it is possible to calculate two independent values for the angle θ, the tilt of the quinol molecule axis to the *c* plane. One value depends on *a* and the other on the *c* dimension only as shown in Fig. 1. The values of θ so calculated are given in Table III. Most of the values found are in good agreement and support the assumptions made. Small discrepancies, however, occur with the carbon dioxide and the methyl cyanide compound and may be interpreted as shown below in terms of the general packing arrangements in the cavities.

FIG. 2.



Schematic representation of the enclosure of a molecule between two cage systems. Increase in length of the enclosed molecule is accompanied by an extension of the cage in one direction and contraction in the plane at right angles without alteration in size of the cage-forming components. For clarity only one enclosed molecule is shown with its immediate surroundings. To correspond with the real structure each cage should be imagined as indefinitely repeated in three dimensions by the prolongation of its edges.

TABLE III.

M.	θ, calc. from *a*.	θ, calc. from *c*.	M.	θ, calc. from *a*.	θ, calc. from *c*.	M.	θ, calc. from *a*.	θ, calc. from *c*.
HCl	*42° 10′	41° 40′	MeOH	42° 21′	42° 18′	MeCN	47° 36′	49° 10′
HBr			H·CO$_2$H ...	43 37	43 14	SO$_2$ (*B*)	43 2	42 46
H$_2$S			SO$_2$	44 36	44 41	SO$_2$ + MeOH	44 5	44 2
C$_2$H$_2$	41 42	41 28	CO$_2$	45 46	44 55	SO$_2$ + HCl	43 12	42 13

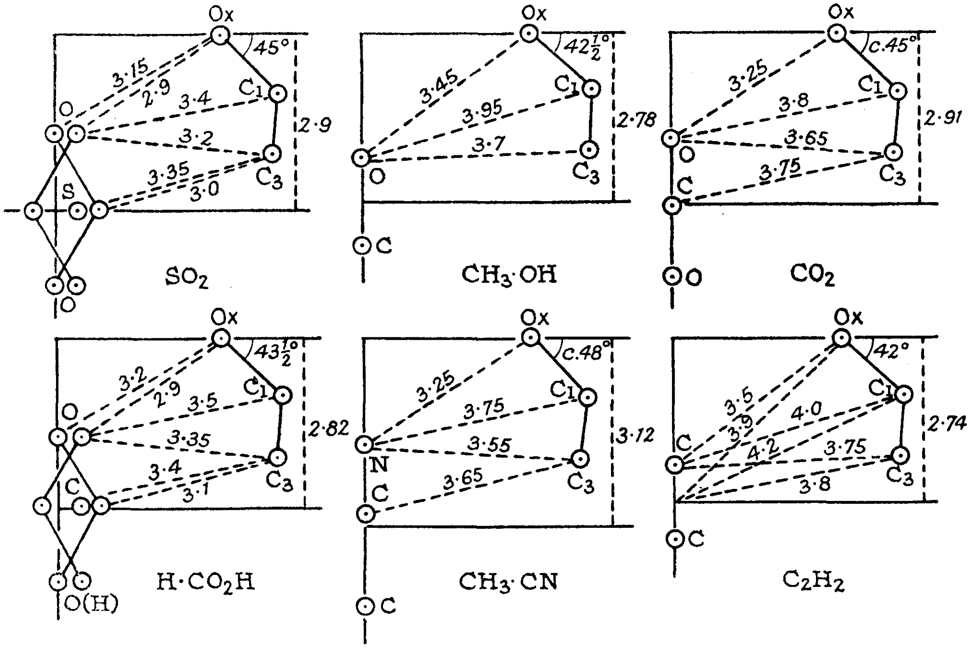
* For these three very similar unit cells the average dimensions $a = 16{\cdot}57$, $c = 5{\cdot}48$ were used.

Approximate interatomic spacings between quinol and the added molecule are shown in Fig. 3. The distances have been obtained graphically on the assumption that there is a stationary molecule of known dimensions in a central position in the cavity of size determined by the appropriate unit-cell dimensions.

In the diagram for the acetylene compound the distances to the middle of the acetylene molecule may be taken as very nearly equal to those applying to the HCl, HBr, and H_2S compounds with $c/2 = 2{\cdot}8$ A. For the bent SO_2 and H·CO_2H molecules alternative sets of values are given for molecules as shown at a given point of their rotation about a vertical axis taken either through the oxygen atoms or between the three atom centres. For the $SO_2(B)$ specimen the distances as given above for SO_2 are, read from top to bottom, modified to 3·1, 2·85, 3·45, 3·3, 3·4, 3·05 A. The quinol molecule has been constructed with the calculated tilt to the *c* face but with an assumed constant angle of 45° between the plane of the benzene ring and the $(\bar{1}2\bar{1}0)$ plane. This angle is not constant but is sufficiently near for the present purpose.

The plane of the benzene rings is found to be at 45° to the $(\bar{1}2\bar{1}0)$ plane in the sulphur dioxide compound which has a *c* spacing about half-way between the extreme observed values for the other compounds. If the quinol cage is compressed along the *c* axis from this position it would be expected from packing requirements that the quinol molecules would twist about their oxygen–oxygen axis to take up a greater angle with this plane and that ultimately an equilibrium determined by the contacts of the quinol molecules would be attained, and this appears to be the case from the nearly constant cell dimensions for the HCl, HBr, H_2S, and C_2H_2 compounds, where there is considerably more room than is necessary to accommodate these small molecules. If, on the other hand, the structure is elongated along the *c* axis it seems likely that in order to give the best all round interatomic spacings the quinol molecules would twist in the opposite direction and so turn into the cavities. Such an extension gives a structure of poorer packing, the unit cell volumes for cells of $a = 16{\cdot}56$, $c = 5{\cdot}47$ (mean values for the most compressed) and for the sulphur dioxide compound $a = 16{\cdot}29$, $c = 5{\cdot}81$ being 1299 and 1335 $k\text{X}^3$, respectively. This extension will therefore only be stabilised by restoring forces supplied by a suitably sized molecule retained in the cavities. The limit of permissible extensions appears to be reached in the methyl cyanide compound, and it is significant that this is the only one of the compounds examined in which the 3 : 1 molecular ratio of the components is attained, stability being obtained in this case only by the filling of all the cavities. This compound alone of those examined showed signs of decomposition, in that some powder lines were observed on the *X*-ray photographs, and it was found impossible to prepare a compound containing the slightly larger carbon disulphide molecule. The discrepancy in the two calculated values for the angle of tilt of the quinol molecule in the methyl cyanide compound may be removed if a slight increase in the hydrogen-bond length to 2·8 A. is assumed, whereby the angle calculated from *a* becomes 49° 0′

FIG. 3.



in sufficient agreement with 49° 10′ calculated from *c*. The discrepancy could also be removed if a slight puckering of the hydrogen-bonded hexagon was assumed. The first explanation seems the more likely since, as discussed above, the benzene rings probably turn in towards the cavities with a consequent tendency to lower interatomic distances than those shown in Fig. 3 (based on a 45° angle to the $\bar{1}2\bar{1}0$ plane); these lower interatomic distances could be most readily corrected by an extension of the hydrogen bonds.

In the carbon dioxide compound, although the molecule is linear and has an oxygen to oxygen distance less than that of the sulphur dioxide molecule, the *c* dimension is about the same as that of the sulphur dioxide compound but the *a* dimension is somewhat lower. The corresponding discrepancy in the angles of tilt of the quinol molecule calculated for the carbon dioxide may be corrected if the hydrogen bond length is assumed to be reduced to 2·72 A. The reduction is possible because the quinol molecules can move slightly in towards the *c* axis without getting too near to the carbon dioxide molecules and, at this *c* dimension and quinol orientation, without bringing the quinol molecules themselves too close together. That this lower hydrogen-bond length does not occur in any of the other compounds is due to the other limitations imposed by interatomic distance of quinol to quinol or enclosed molecule to quinol.

The birefringence may be explained qualitatively in terms of the structure. Since the symmetrical arrangement of molecules in compensating orientations produces uniaxial optical behaviour it is only necessary to consider polarisation parallel and perpendicular to the *c* axis. The direction of greatest polarisation of the quinol molecule will be along the oxygen–oxygen axis, and since this is tilted at about 45° to the *c* axis it tends to produce equal refraction for vibration along the *c* axis and at right angles to it. The other direction of comparatively high polarisability will lie in the plane of the benzene ring at right angles to the oxygen–oxygen axis, but the rotation in the structure of this plane through 45° from a position parallel with the *c* axis has a similar equalising effect and the result is a very low birefringence for the quinol structure as a whole. Two structural alterations which occur as the enclosed molecule M is varied both produce a similar effect on the double refraction which is in agreement with observation. The distension of the cage structures by the trellis effect mentioned above increases the angle above 45° and thus tends to increase the polarisation parallel to the *c* axis. The molecules which produce this distension are themselves arranged with their long directions parallel to the *c* axis and thus also tend to increase the polarisation for a vibration with the electric vector in this direction, *i.e.*, the two effects both contribute to increasing positive character of the double refraction. This is in accordance with the observations recorded in Table I, where the double refraction for the compounds with HCl, HBr, H_2S, C_2H_2, and MeOH has a weak negative value, and that for compounds with $H{\cdot}CO_2H$, SO_2, and MeCN which have a greater *c* : *a* ratio is positive with a maximum value for the most distended structure, that containing methyl cyanide.

EXPERIMENTAL.

The materials used were prepared as follows, each *compound* being described under the heading of the enclosed molecule.

Sulphur dioxide. A steady stream of sulphur dioxide was passed through a saturated aqueous solution of quinol at room temperature.

Sulphur dioxide, specimen (*B*). This substance was obtained by accident in conditions similar to those employed in the preparation of the normal sulphur dioxide compound but with a solution not saturated with sulphur dioxide. More precise details are not known.

Methanol. By crystallisation of quinol from methanol at ordinary temperatures.

Methyl cyanide. By crystallisation on cooling from a warm saturated solution of quinol in methyl cyanide.

Formic acid. By crystallisation on cooling from a warm saturated solution of quinol in A.R. formic acid of concentration exceeding 95%. Any appreciable dilution of the formic acid with water results in the formation of α-quinol.

Carbon dioxide. About 2 g. of solid carbon dioxide were added to 10 ml. of an aqueous solution of quinol, saturated at 40°, contained in a Parr bomb. The cover was secured, and the bomb heated to 50° and then allowed to cool slowly to room temperature. After a short time, the bomb was then opened, and the crystalline product separated.

Hydrogen chloride. By crystallisation from a saturated solution of quinol in ether after saturation with hydrogen chloride at 20°.

Hydrogen bromide. This was prepared as for the hydrogen chloride compound except that the degree of hydrogen bromide saturation was uncertain owing to the formation of an ether–HBr complex.

Hydrogen sulphide. By crystallisation from a saturated aqueous solution of quinol after saturation with hydrogen sulphide at 30°.

Acetylene. Acetylene was passed through a saturated solution of quinol in ether.

Sulphur dioxide + methanol. By crystallisation of a saturated solution of quinol in methanol after saturation with sulphur dioxide at 20°.

Sulphur dioxide + hydrogen chloride. Sulphur dioxide and hydrogen chloride were passed into a solution of quinol in ether saturated at 20°. As soon as precipitation started both gas streams were cut off, and crystallisation was allowed to continue slowly on standing.

Analyses.—When sufficient of the compound was available, analysis was carried out for the added component. Whenever possible the method used was specific for the added component and depended for its application on the liberation of this component in solution.

Sulphur dioxide. The whole of the sulphur present was estimated after destruction of organic matter.

Methanol. The methanol was separated from the bulk of the quinol by distillation as its azeotrope with water and was determined in the distillate by isothermal diffusion into acid dichromate solution and back titration with thiosulphate.

Sulphur dioxide (*B*). The sulphur dioxide was removed from the compound by solution in water and distillation in an evacuated apparatus where it was absorbed in sodium hydroxide solution and determined by means of standard iodine.

Methyl cyanide. The nitrogen was determined by the micro-Kjeldahl method.

Formic acid. The compound was dissolved in water, and the liberated formic acid titrated with standard alkali. Although any excess of alkali reacts with the quinol this does not occur until the acidity has been neutralised, the end-point to phenolphthalein being readily observed.

Carbon dioxide. The method was similar to that described for sulphur dioxide (*B*) except that the carbon dioxide was absorbed in sodium hydroxide + barium chloride solution and the barium carbonate so precipitated was determined.

Hydrogen chloride. The compound was dissolved in water and the liberated chloride ion determined as acidity or by electrometric titration with standard silver nitrate solution.

Hydrogen bromide. The bromide ion liberated on solution was determined on the micro-scale by means of standard silver nitrate with mercuric chloride + diphenylcarbazone as internal indicator in an ether layer.

Hydrogen sulphide. As for sulphur dioxide (*B*) except that the distillate was not neutralised before addition to acidified iodine solution.

Acetylene. No quantitative analysis was made. The presence of acetylene in appreciable concentration was confirmed by precipitation of copper acetylide.

Sulphur dioxide + methanol. The sulphur dioxide was determined as acidity and the presence of methanol was confirmed by distillation from a neutralised solution.

Sulphur dioxide + hydrogen chloride. Total acidity and chloride were determined.

Each compound was examined under the polarising microscope and, where well-formed crystals were obtained, a morphological examination was made by Miss M. W. Porter. The principal refractive indices were determined by the temperature index variation method. Densities were found by flotation. The unit-cell dimensions were determined from oscillation photographs taken with copper-K_α radiation and the resultant photographs were in each case compared with those of the sulphur dioxide and the methanol compound previously examined in detail.

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