

50. The Structure of Molecular Compounds. Part III. Crystal Structure of Addition Complexes of Quinol with Certain Volatile Compounds.

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A detailed determination, mainly by three-dimensional Fourier methods, has shown that in the compounds considered quinol molecules link together through hydrogen bonds to form infinite three-dimensional complexes of trigonal symmetry. The resulting giant molecule has a form, imposed by the dimensions of the quinol molecule and the disposition of the hydrogen bonds, so open that two such giant molecules are built up completely interpenetrating each other but having no direct attachment. In cavities enclosed simultaneously by the two giant molecules are located the molecules of the second volatile component which cannot escape from its surroundings. The composition $3C_6H_4(OH)_2.M$ is determined by the number of spaces available for the second molecule M. For the case where M is sulphur dioxide the co-ordinates of all atoms of the quinol framework have been found. The position of the sulphur dioxide and its rotation about one axis have also been established by Fourier analysis. In the quinol molecules the interatomic distances found (to within about ± 0.03 Å.) are C-C 1.39, C-O 1.36, OH...O 2.75 Å. The hydroxyl groups are arranged in hydrogen-bonded hexagons. The analysis involves some special applications of Patterson methods which here are able to establish the presence of a symmetry centre and to locate most of the atoms in a direct manner.

IN addition to the usual type of molecular compound formed by phenols with other substances such as aldehydes, quinol forms a series of complexes with certain volatile compounds of the general type 3(or 4) $C_6H_4(OH)_2.M$, where M denotes the second molecule, *viz.*, H_2S (Wohler, *Annalen*, 1849, **69**, 297), SO_2 (Clemm, *ibid.*, 1859, **110**, 357), $H\cdot CO_2H$ and HCN (Mylius, *Ber.*, 1886, **19**, 999), HCl (Schmidlin and Lang, *ibid.*, 1910, **43**, 2817), HBr (Gomberg and Cone, *Annalen*, 1910, **376**, 238), $CH_3\cdot OH$ (Palin and Powell, *Nature*, 1945, **156**, 334), $CH_3\cdot CN$ (*idem*, unpublished). These compounds are very stable under ordinary conditions of storage, and have no smell of the volatile substance, but are decomposed into their components when heated to near their melting points or dissolved in water. Mylius (*loc. cit.*) from a series of experiments with the formic acid complex concluded that no ordinary chemical combination exists. He suggested that during crystallisation the quinol molecules were somehow able to lock the volatile component in position. It was thought that the crystal structure of this class of compound would be of interest in that it would show the way in which the second component is retained and at the same time give some information on the structure of quinol itself. This communication is mainly concerned with a detailed determination of the structure of the complex with sulphur dioxide.

Crystals of the compound were prepared by slow crystallisation from a solution of quinol

in water which was saturated with sulphur dioxide. Chemical analysis gives a somewhat lower sulphur dioxide to quinol ratio than the 1 : 3 value given by Clemm (*loc. cit.*), suggesting that this is not a stoichiometric compound. The point is discussed further below. The compound, stable at room temperature, has no smell of sulphur dioxide which is, however, set free quantitatively when the substance is dissolved in water, alcohol, or ether, or heated to the melting point. A trace of sulphur dioxide, detectable by smell, is given off from the material ground in a mortar.

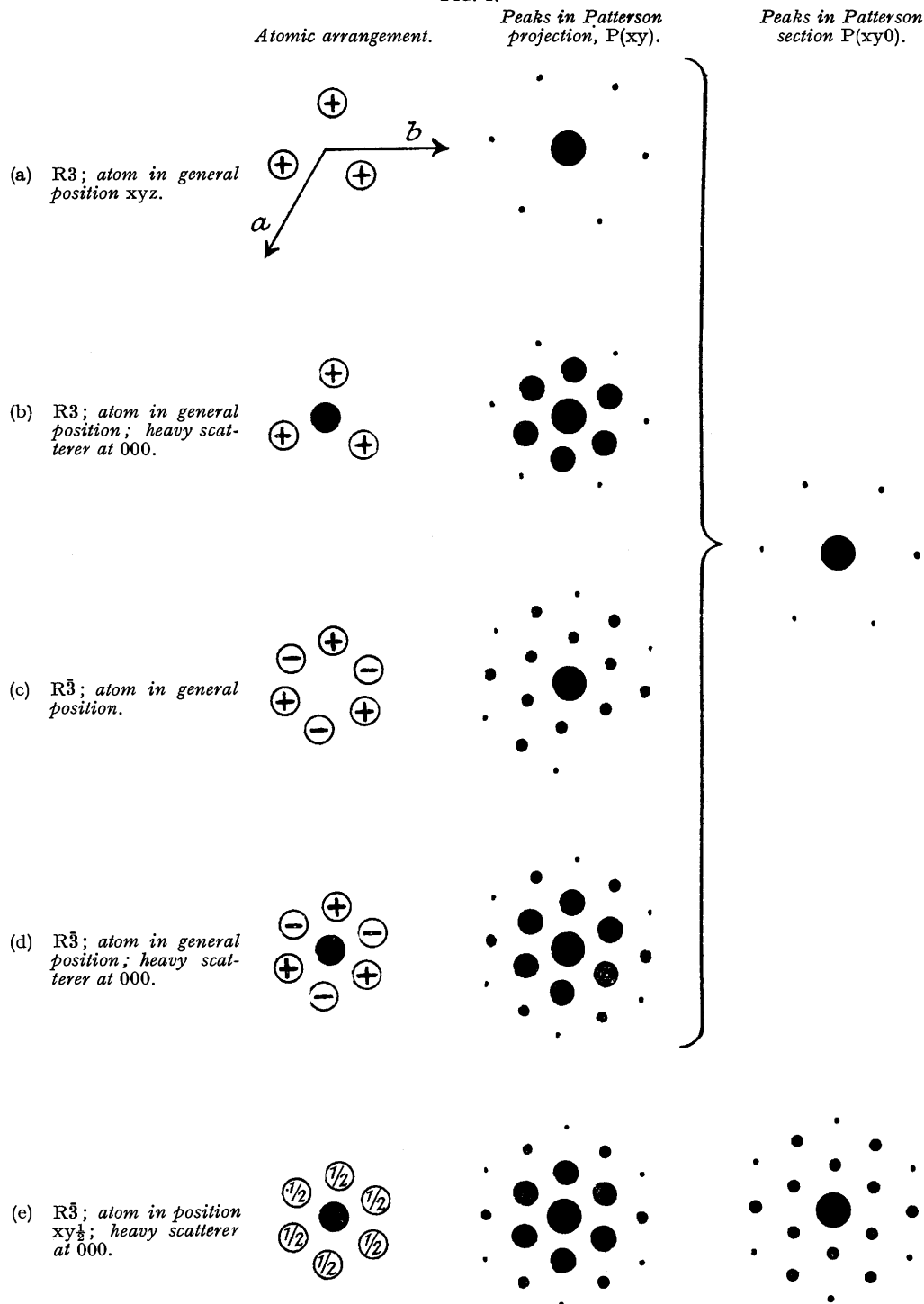
The yellow crystals form six-sided prisms of the form $\{11\bar{2}0\}$ terminated by rhombohedral faces $\{10\bar{1}1\}$. They are optically uniaxial with weak positive birefringence and are harder than most organic crystals. The unit cell dimensions found were $a = 16.29 \pm 0.03$, $c = 5.81 \pm 0.02$ kX referred to hexagonal axes, or $a = 9.6$ kX, $\alpha = 116\frac{1}{2}^\circ$ referred to rhombohedral axes. The density 1.440 ± 0.005 g./c.c., determined by flotation, gives a molecular weight of 1165. This corresponds approximately to three molecules of $\text{SO}_2, 3\text{C}_6\text{H}_4(\text{OH})_2$ per hexagonal unit cell (equivalent to one molecule per rhombohedral cell).

Oscillation photographs taken about axes perpendicular to (0001), $(11\bar{2}0)$ and $(10\bar{1}0)$ showed a characteristic appearance due to absence of spectra $h - k + l \neq 3n$ which established the rhombohedral lattice, and lack of vertical planes of symmetry, as shown by a [0001] zero layer line Weissenberg photograph, reduced the space-group possibilities to $R\bar{3}$ or $R3$ which differ in that $R\bar{3}$ has a centre of symmetry and $R3$ has not. Although there are similar rhombohedral faces at each end, the centrosymmetric nature of the crystals was at first open to doubt since "β-quinol" (Caspari, *J.*, 1927, 1093) which also has $(11\bar{2}0)$ prisms, very similar cell dimensions and (as reported) nine molecules of quinol per unit cell, has, in contrast, dissimilar terminal faces which point to the absence of a symmetry centre. But tests for piezoelectricity by a modification of the Giebe and Scheibe circuit (*Z. Physik*, 1925, **33**, 760) and for pyroelectricity by the liquid-air method (Martin, *Min. Mag.*, 1931, **22**, 519) gave negative results with the sulphur dioxide compound and it was considered reasonable to assume the space-group $R\bar{3}$ for purposes of an attempted direct solution. The stages of the subsequent analysis are not, however, based on the assumption of centrosymmetry but are used to confirm it. Since the only electron-density projection expected to give useful information was that seen along the c axis, it was decided to use three-dimensional methods where necessary. Equi-inclination Weissenberg photographs were therefore taken about the [0001] axis of small crystals of approximately cylindrical shape. The required intensity range was covered by means of two exposures and multifilm technique (de Lange, Robertson, and Woodward, *Proc. Roy. Soc.*, 1939, *A*, **171**, 404). Copper- K_α radiation was used. Intensities, estimated visually and correlated for different layer lines by factors obtained from photographs about other axes, were divided by their corresponding Lorentz polarisation-rotation factors to give a set of F^2 and hence F_{hkl} values. In this way relative F^2 and F values were obtained for nearly 200 hkl , with orders of h and k up to 19 and l up to 3, and $10^{-8} \sin \theta/\lambda \gtrsim 0.6$. Each of these was included the required number of times with different but related indices in any Fourier summation.

The space-group requirements of $R\bar{3}$ as they affect this compound are as follows. Since there are nine molecules of quinol per unit cell, their centres must lie in special positions $\frac{1}{2}0\frac{1}{2}$, $0\frac{1}{2}\frac{1}{2}$, $\frac{1}{2}\frac{1}{2}\frac{1}{2}$, with the equivalents at $+$ ($\frac{2}{3}\frac{2}{3}\frac{2}{3}$) and $+$ ($\frac{1}{3}\frac{1}{3}\frac{1}{3}$), and the asymmetric unit consists of one half of the centrosymmetric quinol molecule. The non-centrosymmetric sulphur dioxide molecule with $\widehat{\text{OSO}}$ angle $\approx 120^\circ$ cannot as a whole fit into the space-group unless it is rotating or molecules take up various orientations in different cells to give statistically the $R\bar{3}$ symmetry. The sulphur atom alone could be placed in the threefold position at the origin or the oxygen atoms in a sixfold position at $\pm 00z$, but these conditions together would require a linear sulphur dioxide molecule. For a rotating molecule the space-group symmetry may be satisfied in several ways. With sulphur at the origin the oxygens must revolve round the c axis to give the trigonal symmetry, and if they remain in planes at $\pm z$ an effective symmetry centre is also introduced. If, instead, the oxygen atoms are placed at $\pm 00z$ the sulphur atom then moves over a circle round the c axis at $z = 0$. If neither sulphur nor oxygen occupies fixed positions rotation about an axis, *e.g.*, through the centre of gravity of the molecule such that all atoms describe circles round the c axis, sulphur at $z = 0$ and oxygen at $\pm z$, produces the same symmetry. These are the minimum requirements but other rotations and oscillations may be superposed.

Since it thus appears that the sulphur dioxide molecule would lie, as a whole, close to the c axis an attempt was made to obtain an approximate electron-density projection perpendicular to this axis by assuming the space-group $R\bar{3}$ and giving all the F_{hkl0} values the positive sign.

FIG. 1.

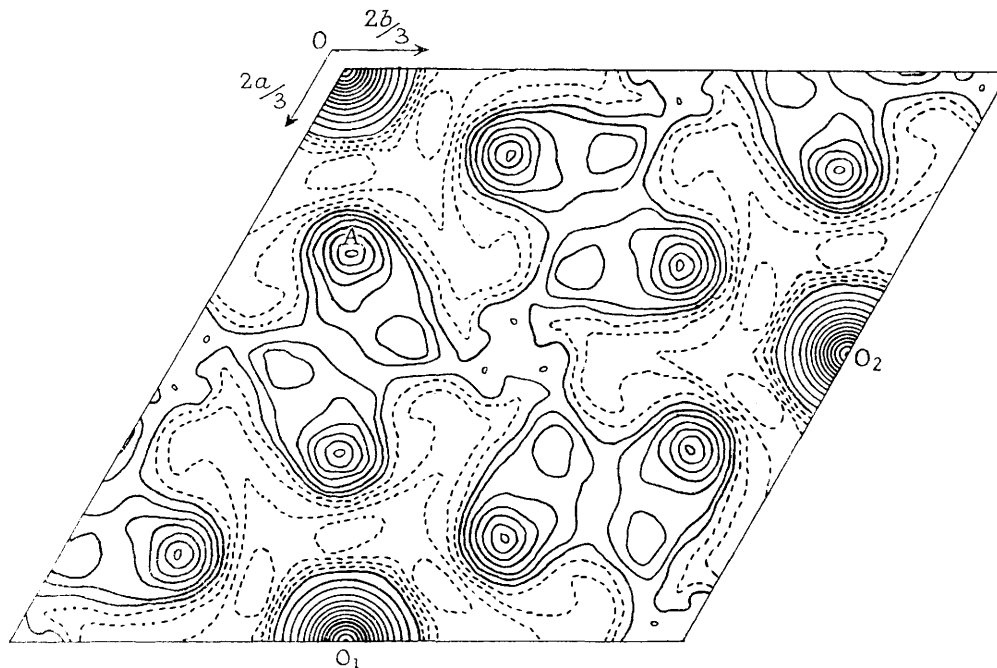


The peaks have heights indicated qualitatively by their areas. The experimental Pattersons agree with arrangement (e) but the outermost peak is enhanced owing to overlap effects. The extreme height of the innermost set of peaks in the projection is subsequently found to be due not only to the presence of the heavy scatterer at the origin but to the fortuitous placing of quinol oxygen atoms at points (corresponding to the \bar{A} peaks) approximately at $\frac{1}{3}$ and $\frac{2}{3}$ along the line joining two sulphur dioxide centres. This causes considerable overlap of oxygen-oxygen and other vectors with the peak due to the sulphur dioxide-oxygen vector.

The structure factor contributions of the sulphur dioxide will be positive for all except high indices, and it was possible that they might have been large enough to outweigh the effects of the lighter atoms for so many reflexions that the positions of other atoms would be indicated in the first approximate electron-density projection so obtained. From the resulting projection it appears that the structure could have been found in this way, but in view of doubts concerning the space-group it was decided to develop it afresh by application of Patterson (*Z. Krist.*, 1935, **90**, 517) and Harker (*J. Chem. Physics*, 1936, **4**, 381) F^2 Fourier synthesis, without the initial assumption of centrosymmetry.

Although the total number of peaks in the Patterson synthesis of a quite simple structure is very large, and interpretation is commonly difficult, there is sometimes a small region close to the origin where the peaks due to a single atom, symmetrically repeated in some way around the origin, may be observed comparatively free from distortion by other peaks. This may be expected when these atoms are linked at a short distance, and when for structural reasons it is impossible for any other set of linked atoms to be separated at the same or nearly the same

FIG. 2.



Patterson-Fourier projection $P(xy)$ on (0001). The interval between full contour lines near the origin is twice that used elsewhere.

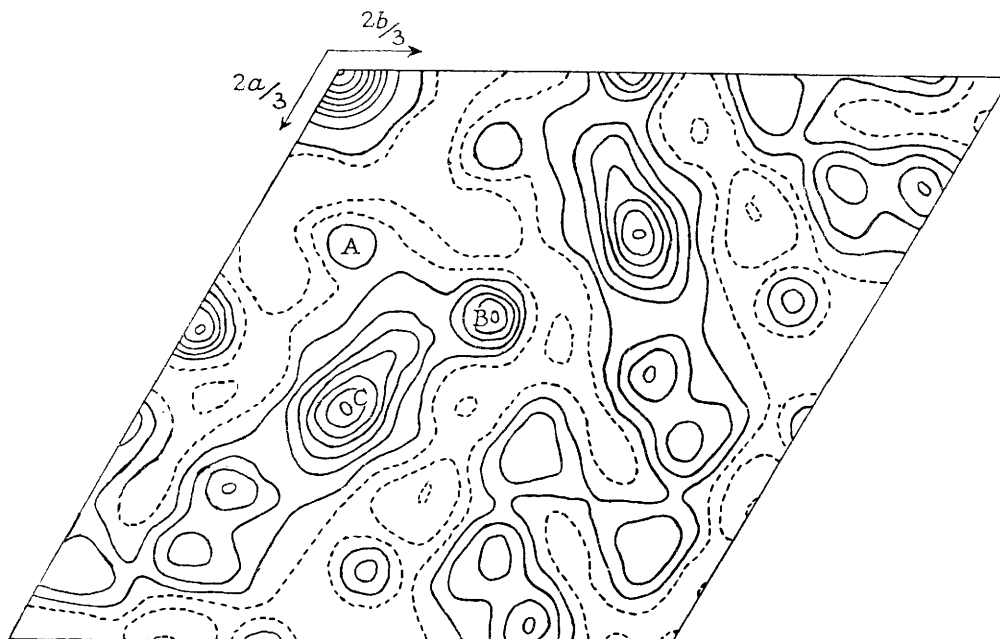
distances in similar directions. In Fig. 1 are shown the sets of Patterson peaks to be expected in a projection perpendicular to the c axis, and in a parallel section of the three-dimensional Patterson synthesis at $z = 0$. A single atom with its space-group equivalents is considered, and peak patterns for $R\bar{3}$ and $R\bar{3}$ with and without the effect of a large scattering mass near to the c axis are indicated.

The Patterson projection as computed from observed F_{hkl0}^2 is reproduced in Fig. 2. It shows very high peaks A lying at one-third intervals nearly on lines joining the two origin peaks O and O_1 . There is a fairly high plateau between the two A peaks and comparatively little elsewhere. There are combined together in this projection the effects of several light atoms and the heavy scattering sulphur dioxide which will give a number of superposed patterns similar to those in Fig. 1, together with other peaks due to interatomic vectors between atoms unrelated by symmetry. The great height of peaks A shows clearly that the structure must contain the heavy scatterer on the threefold symmetry axis as in (b), (d), or (e). The plateau suggests that the quinol molecules are placed somehow along lines joining the several pairs of origins, and the small peaks near the centre of Fig. 2 at B such that OB makes an angle of 30° to OA and $OB =$

$\sqrt{3}0A$ correspond to peaks that arise in (b), (c), (d), or (e) if there is an atom in a position corresponding to A.

In a Patterson section with $z = 0$, interatomic vectors between groups of three atoms related by the symmetry axis should produce sets of peaks similar in pattern to those shown in (a), and the overwhelming influence of the sulphur dioxide should be removed, since it can produce peaks in this section only in co-operation with any atoms which are accidentally at the same z level. In the computed section, Fig. 3, there are peaks A of an inner hexagon as required for (a), (b), (c) or (d), but there are also peaks B and C in positions similar to the additional peaks in the projections (but not the sections) for (c) and (d). The peak c may in part be due to vectors between sulphur dioxide and some part of the quinol molecule which, as previously found, must lie in this general direction, but B cannot be so explained and must therefore be due to lighter atoms only. Since it lies in the required direction at $\sqrt{3}$ times the distance of A from the origin, the simplest interpretation is that there is a planar group of six atoms in a regular hexagon in positions corresponding to the A peaks around the c axis. This will arise if the space-group is

FIG. 3.



Patterson-Fourier section $P(xy0)$. The interval between full contour lines near the origin is four times that used elsewhere.

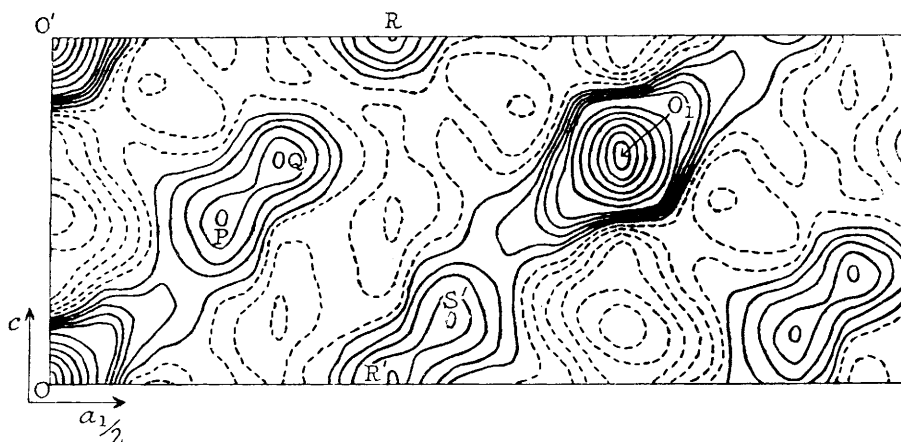
$R\bar{3}$ and the z co-ordinate of the atoms concerned is 0 or $\frac{1}{2}$. This inner hexagon has a side of approximately 2.8 Å., such as would be expected for a set of six OH groups hydrogen-bonded in this form. Peak A may not give the exact position of the oxygen atoms since it may be distorted by nearby peaks due to other atoms.

If the sulphur dioxide molecule is rotating so that its centre is in the threefold position 000, the hexagon of oxygen atoms must be at $z = \frac{1}{2}$ because the relatively low height of the peak A in the Patterson section shows that the sulphur dioxide and the six oxygen atoms are not at the same z level. The greater height of peak B must be due to accidental overlapping with a peak due to some other pair of atoms, and the magnitude of the complex peak C suggests that it arises from vectors between sulphur dioxide and parts of the quinol molecules having the same z co-ordinates. The structure therefore appears to consist of quinol molecules arranged so that each oxygen atom lies on one corner of a hexagon round a trigonal axis, with the benzene ring connecting pairs of oxygen atoms which lie near different axes. Part of each quinol molecule will lie in or near a plane parallel to the c axis and passing through the origins O and O_1 (Fig. 2), and there should be important vectors between these parts and the sulphur dioxide molecule which is also contained in this plane. The Patterson-Harker section prepared after

transformation of the indices to orthohexagonal axes is for convenience plotted with reference to axes X_1YZ , where X_1 makes an angle of 30° with the original X axis. The section (Fig. 4) shows peaks $PQRS$ on a line joining the origin O to the origin O_1' at $z = 1\frac{2}{3}$, $PQ = RS \approx 1.4$, $QR \approx 2.8$ Å. Consideration of the probable size and shape of the quinol molecule leads to the conclusion that P gives the vector from the sulphur dioxide at the origin and the quinol oxygen atom, and Q gives the similar vector to the carbon atom to which this oxygen is attached. The simplicity of the pattern without other peaks shows that the quinol molecule is symmetrically placed between O and O_1' and thus again introduces a symmetry centre. The other four carbon atoms of the quinol molecule are necessarily out of the plane of this section.

The detailed structure could now be determined, and the final values of the parameters which give the positions of all atoms in the unit cell were reached in four successive stages described in more detail below. The Patterson analysis fixes the approximate position of the O-O axis of the quinol molecule, and the first set of co-ordinates was derived by selection of values in agreement with this and the further conditions that the quinol molecules must be hydrogen-bonded in such a way as to accommodate the sulphur dioxide molecule near to the origin, the O-C distance by analogy with that in resorcinol (Robertson, *Proc. Roy. Soc.*, 1936, *A*, 157, 79; 1938, 167, 122) should be about 1.36, the benzene ring a flat hexagon of side approximately 1.39, and the separations of non-bonded atoms not much less than 3.5 Å. Within limits

FIG. 4.



Patterson-Fourier section $P(x,0z)$. The interval between the innermost seven contours near the origin is four times that elsewhere.

imposed by these conditions co-ordinates were selected by comparison of calculated structure factors with the observed values. These calculated values depend on the inclusion of a contribution for the sulphur dioxide molecule. The preliminary estimates of this quantity were sufficiently accurate to give a substantial number of correct signs for the structure factors, and the subsequent stages all consisted of electron-density Fourier syntheses in which signs were revised or previously uncertain terms were included as the revised co-ordinates of the preceding stage permitted.

(1) Structure factors F_{hki0} were calculated for structures in which the O-O axis of the quinol molecules was fixed as described above, the sulphur dioxide contribution was calculated for a sulphur atom at the origin with two oxygen atoms imagined uniformly distributed over the surface of a sphere of radius 1.45 Å, equal to the S-O bond distance, and the co-ordinates of the carbon atoms which are not fixed by the above considerations were given alternative values corresponding to various angles of twist, relative to the rest of the structure, of the plane of the benzene ring about the O-O axis. This was done for low-order reflexions from contoured structure factor graphs (Bragg and Lipson, *Z. Krist.*, 1936, 95, 323). The atomic scattering factors used were calculated from the data given by Robertson (*Proc. Roy. Soc.*, 1935, *A*, 150, 109) with an approximation for the hydrogen atoms. From the best agreement obtainable in this way a set of xy co-ordinates for all atoms was derived.

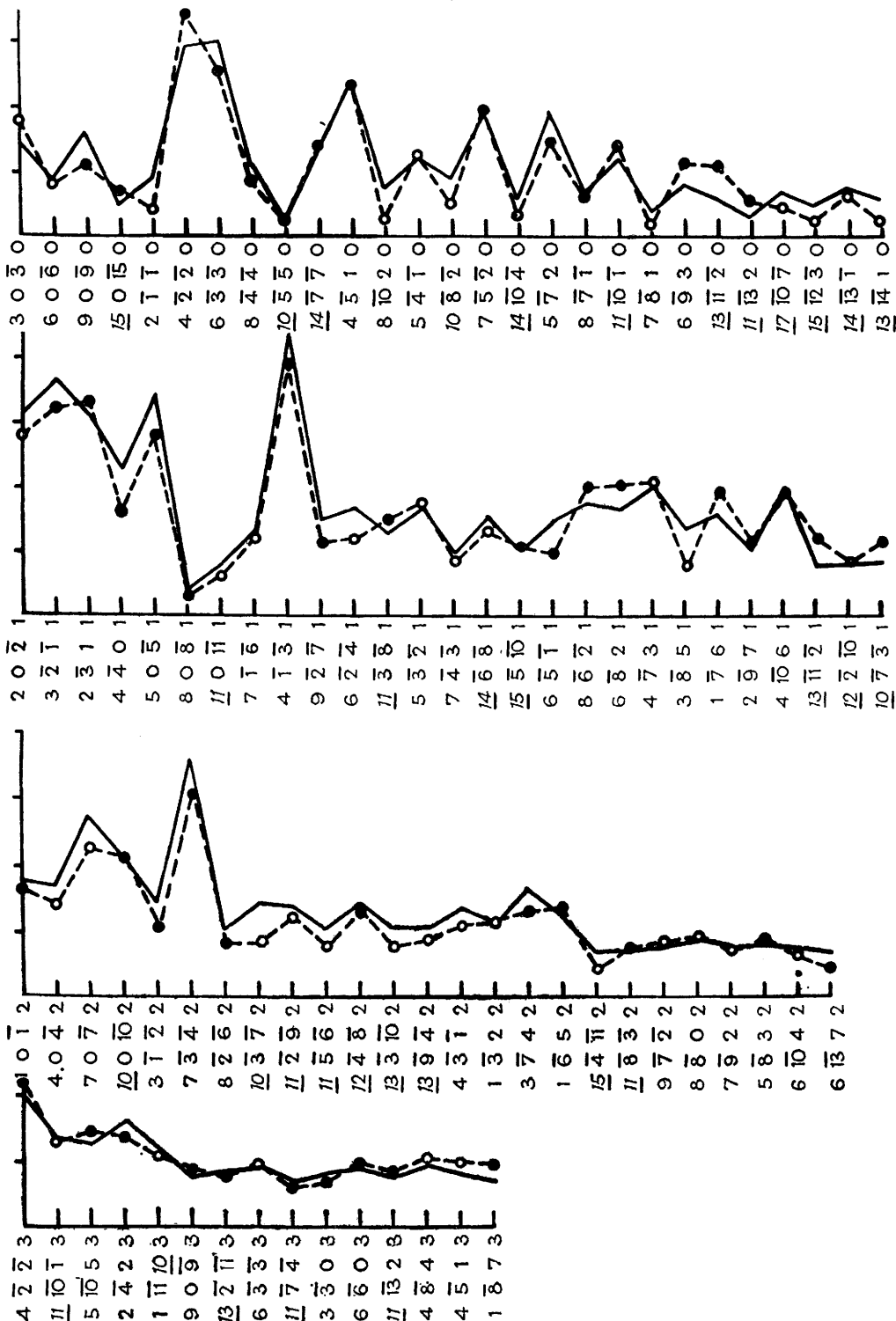
(2) The electron-density projection on (0001) was computed. The calculations of stage (1) provide the signs of F_{hki0} for lower orders but for higher orders, $10^{-8} \sin \theta/\lambda > 0.42$, the compar-

atively large sulphur contribution was presumed to confer the positive sign in every case. From the projection obtained, which showed the sulphur dioxide as a single peak and the form of the quinol molecule without very clear resolution of the atoms, and from consideration of a model to show the general packing arrangements, z co-ordinates were estimated and revised values for xy obtained.

(3) The xyz values obtained in (2) were used to calculate F_{hkl} . The agreement was good for $l = 0$ and $l = 1$, and although it was not so good for $l = 2$ or 3 it was considered probable that the signs would be correct for all except the weak reflexions. All F values above a selected magnitude that seemed large enough to be incapable of sign reversal through any possible errors were therefore given the computed sign, and the remainder, consisting of about a quarter of those with $l = 1$, half of those with $l = 2$ and three-quarters of those with $l = 3$, were omitted from the first set of three-dimensional Fourier summations which were then carried out. By chance, the orientation of the quinol molecules and the rhombohedral symmetry combine to reveal the x and y co-ordinates of all four atoms of the quinol part of the asymmetric unit in suitable areas of the sections through the cell at $z = 0$ and $z = \frac{1}{2}$. The section ZX_1 passes nearly through the centres of carbon atoms C_1, C_1' and oxygen atoms O, O' (see Fig. 11) of the quinol molecule, and a section parallel to this at $y = 0.055$ passes nearly through the centres of the remaining carbon atoms C_2' and C_3 . These four sections were computed and showed resolution of all atoms of the quinol part of the structure so that their combined results made it possible to estimate new xyz parameters for these atoms. An examination of the ZX_1 vertical section which passes through the supposed centre of the sulphur dioxide molecule showed that the peak is lower than would be expected if there were a sulphur atom at the origin, and there is a marked elongation parallel to the c axis. This suggests that the rotational motion of the molecule is about the c axis only, and the shape of the peak suggests that the axis of rotation passes through the two oxygen atoms rather than through the centre of gravity of the molecule.

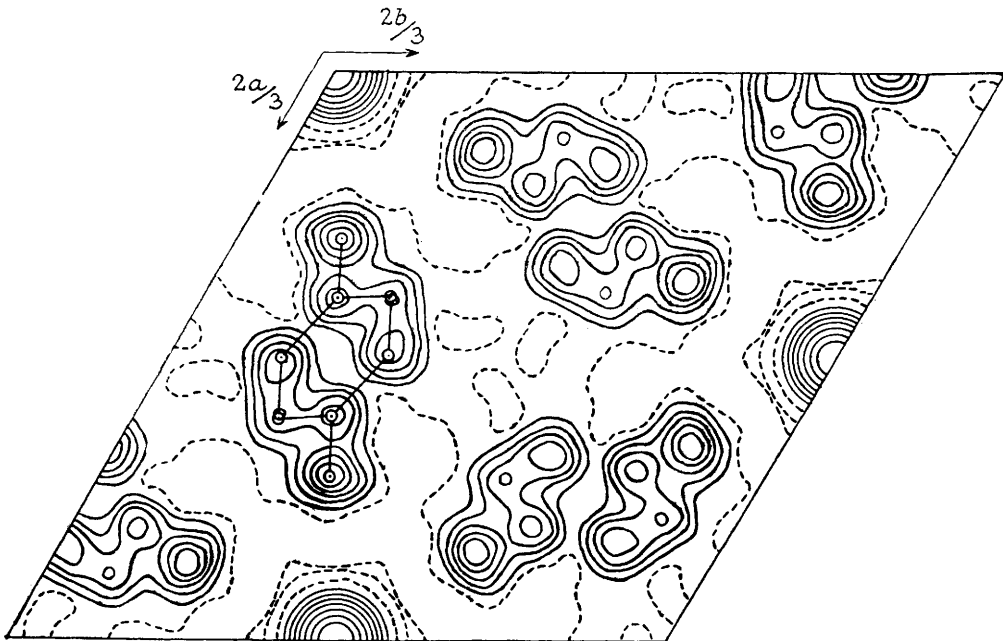
(4) Signs for all observed F_{hkl} were then determined on the basis of the revised co-ordinates for the carbon and oxygen of the quinol part as given by (3) and a modified contribution for the sulphur dioxide. The former approximation gives calculated values of F_{hkl} , especially for $l = 2$ or 3 , showing discrepancies so long as sulphur and the two oxygen atoms are all regarded as associated with the point 000, but the agreement may be improved if sulphur is assumed to be in motion around 000 and the oxygen atoms are treated separately as units near to $\pm 00z$, $z = 0.217$. This supports the conclusions derived from the electron-density sections in (3), but in order not to prejudge the type of motion too precisely the modified sulphur dioxide contributions were estimated by a method designed, as far as could be seen, to give the correct signs of the F_{hkl} irrespective of the exact motion of the atoms around these points. If an atom may be considered owing to its motion as uniformly distributed over some domain having a centre of symmetry at xyz , its contribution to the structure factor F_{hkl} is given by the expression $f' \cdot e^{2\pi i(hx + ky + lz)}$ where f' is the atomic scattering factor f multiplied by a correction term which depends on the form of the uniformly occupied domain. This term is $(\sin z)/z$ for uniform distribution on the surface of a sphere, $z = 2\pi r/d_{hkl}$, r = radius of sphere, d_{hkl} = spacing of the plane for which the contribution is to be calculated. For uniform distribution on a circle of radius r the term is $J_0(z)$, $z = 2\pi r \sin \psi/d_{hkl}$, ψ is the angle between the normal to the circle and the normal to the plane hkl concerned, $J_0(z)$ is the Bessel coefficient of order zero of argument z . When $z = 0$, *e.g.*, for $r = 0$ or $\psi = 0$, the correction term is unity. For both cases mentioned the term changes, as z increases, according to somewhat similar curves; $(\sin z)/z$ first changes from positive to negative at $z = \pi$ and thereafter reverses sign at intervals of π , $J_0(z)$ first becomes negative at z slightly $> \frac{3}{4}\pi$ and thereafter reverses sign at points very close to $\frac{3}{4}\pi + n\pi$. The radius r cannot be large since the space available for these motions is restricted. In consequence r/d_{hkl} and therefore z is generally small and the correction term is a positive number less than unity. Owing to the form of the curves it is impossible to get large magnitudes of the correction term for the comparatively few instances among the high order reflexions where it might be negative. This is also true for any other type of small movement. Since there are also contributions to the structure factors from the fixed parts of the structure it is therefore very improbable that a wrong sign will be obtained if the sulphur and oxygen contributions are computed as though the atoms were at 000 and $\pm 00z$ and then diminished by a suitable factor without change of sign. A constant factor of $\frac{5}{8}$ was found to give a considerably improved agreement in the calculated F_{hkl} values for $l = 2$ or 3 and this itself confirms that the general direction of the modification is correct. The agreement of calculated and observed values for a number of reflexions may be seen from Fig. 5. With the signs thus determined, the projection and all the sections were repeated with inclusion of all the F_{hkl} values which had pre-

FIG. 5.



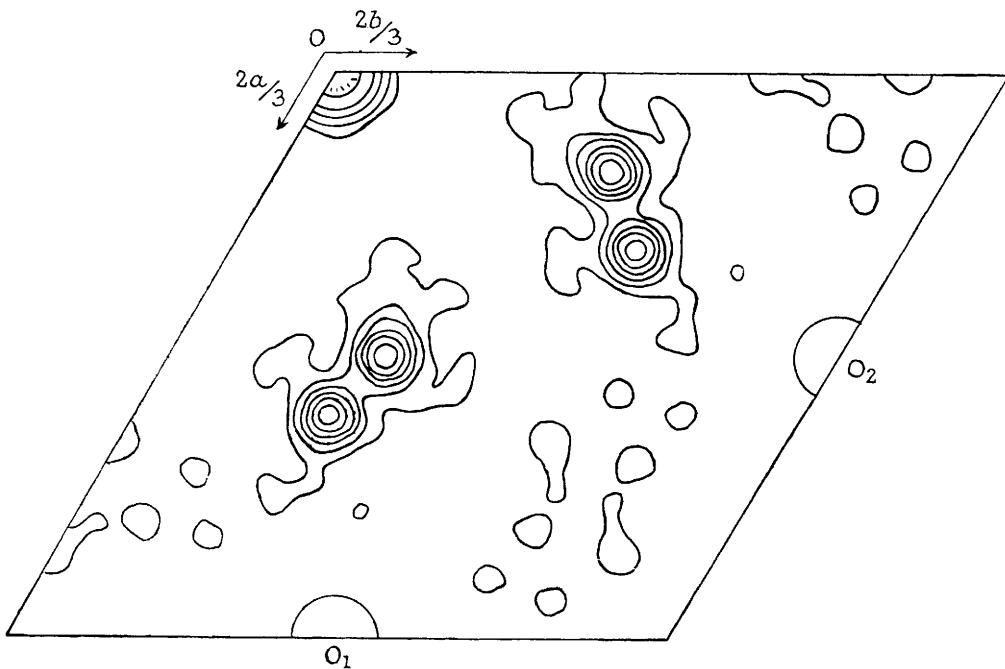
The calculated and the relative observed F_{hkl} values for the principal reflexions reduced to approximately the same scale. — Observed; --- calculated (● positive, ○ negative).

FIG. 6.



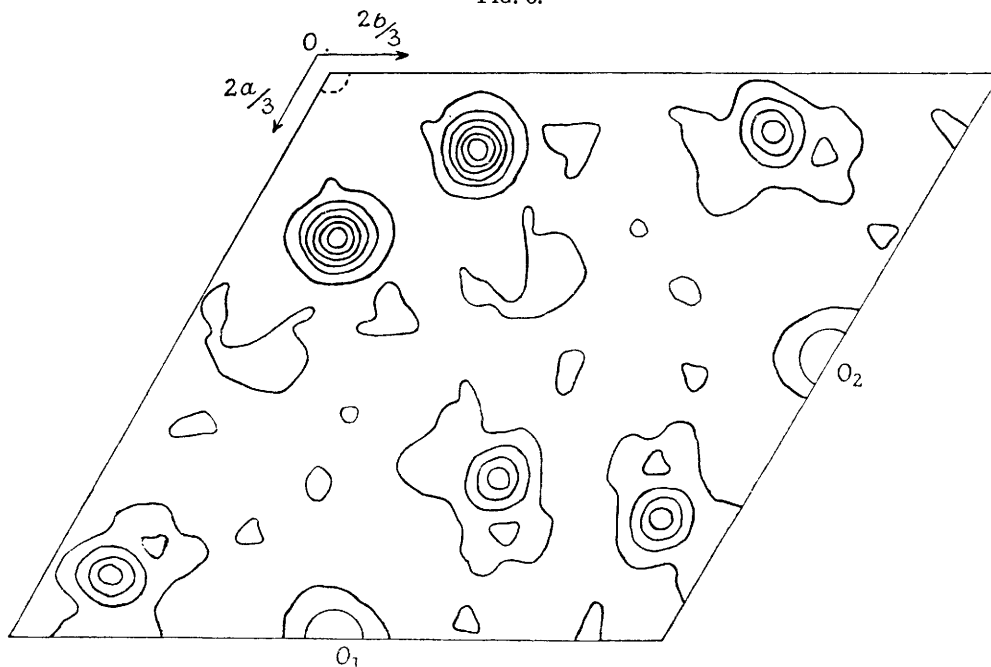
Relative electron-density projection $\rho(xy)$, with atomic positions indicated for one quinol molecule. Sulphur dioxide appears as a single peak of circular symmetry at the origin.

FIG. 7.



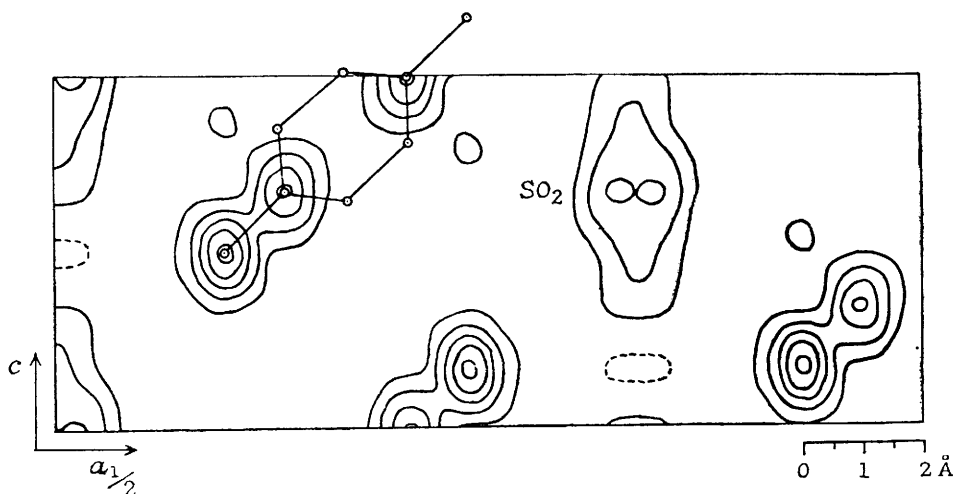
Relative electron-density section $\rho(xy0)$, showing peaks for atoms C_1' and C_2' (see Fig. 11). The irregular areas of low electron density in this section and in that of Fig. 8 are mainly caused by atoms not in the plane of the section. The peak at the origin O has a small central depression, not shown by the contours, and arises from the rotation of the sulphur atom as described in the text. At O_1 and O_2 the section passes near to oxygen of the sulphur dioxide molecule on the side remote from the sulphur and shows a small peak (cf. Fig. 8).

FIG. 8.



Relative electron-density section $\rho(xy\frac{1}{2})$, showing peaks for two oxygen atoms of a hydrogen-bonded hexagon and carbon atoms corresponding to C_3 and C_3' (see Fig. 11). At origin O the section, passing midway between two sulphur dioxide molecules, shows no peak, but at O_1 and O_2 it passes between the sulphur and one oxygen atom of a sulphur molecule and shows peaks. These accordingly have a higher electron density than the peaks in the corresponding positions in Fig. 7.

FIG. 9.

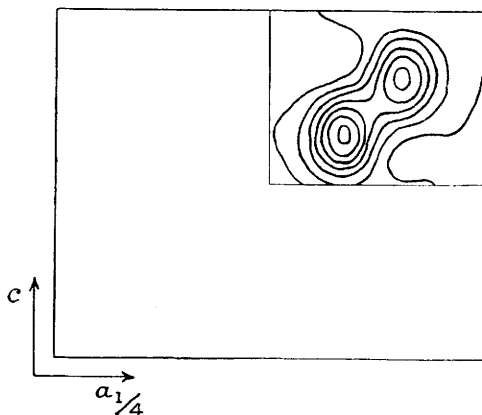


Relative electron-density section (x_1Oz) with peaks for C_1C_1' and for the oxygen atoms O, O' (see Fig. 11). The projected positions of the other carbon atoms which are out of the section are also indicated.

viously been omitted owing to uncertainty of signs. Marked improvements in the resolution and absence of spurious detail (most of the irregular areas of electron density which appear in addition to the principal peaks in Figs. 7 and 8 are due to atoms near the sections) further confirm the correctness of the sign determination. Co-ordinates of the carbon and oxygen atoms of the quinol part of the structure estimated from these new sections accord within narrow

limits with known interatomic distances, and, since they would be affected by any errors in the signs used, the remaining portions of the electron-density maps, calculated from the same experimental F values and the same computed signs, give direct evidence on the position of the sulphur dioxide (see below).

FIG. 10.



Relative electron-density section ($x_1, -0.055, z$) showing peaks for C_2 and C_3' .

Figs. 6—10 show relative electron density for the projection and sections named; Figs. 11 and 12 show the relationship to each other of the nine quinol molecules and the three sulphur dioxide molecules of the hexagonal unit cell. The table gives the parameters for the atoms as found in the four successive approximations.

Atomic parameters as estimated in successive stages of the structure determination.

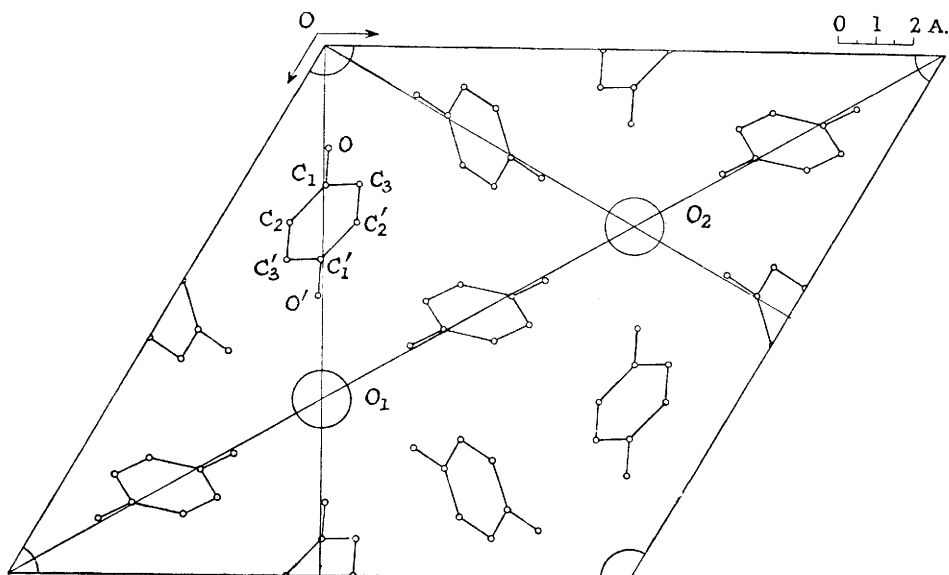
	(1)	(2)	(3)	(4)
Atom.	Patterson's and trial and error calculations of F_{hkl0} .	First F_{hkl0} synthesis (some signs incorrect) and model.	First F_{hkl} syntheses to give sections. Many weak F 's omitted (signs uncertain).	Final syntheses with all F 's. In calculation of signs, second modified form of SO_2 contribution included.
x	0.193	0.198	0.192	0.195
O y	0.106	0.104	0.103	0.105
z	—	0.483	0.500	0.500
x	0.264	0.266	0.262	0.263
C_1 y	0.138	0.135	0.133	0.135
z	—	0.655	0.670	0.665
x	0.345	0.329	0.340	0.334
C_2 y	0.127	0.108	0.117	0.113
z	—	0.646	0.640	0.645
x	0.260	0.270	0.262	0.262
C_3 y	0.181	0.198	0.188	0.188
z	—	0.839	0.850	0.855

These parameters give for the quinol molecule a benzene ring of regular hexagonal form with side 1.39 Å. to within 0.03 Å., and $C-O = 1.36 \pm 0.03$ Å. The $OH \dots O$ distance is 2.75 ± 0.03 Å.

Discussion of the Structure.—The essentials of the structure which are difficult to visualise from the electron-density maps are illustrated in Figs. 13 and 14. In Fig. 13 it may be seen that the quinol molecules, represented for clarity by a single line joining the two oxygen atoms of one molecule, are linked through hydrogen bonds to form a giant molecule infinitely extended in three dimensions. Six oxygen atoms form a plane hexagon of side 2.75 Å. parallel to the xy plane. The central lines of six quinol molecules extend alternately up and down from these oxygen atoms. The oxygen-oxygen axis of the molecule makes an angle of 45° with the plane of the oxygen hexagons, and, owing to an inclination of about 3° to the line joining the corresponding origins, makes two slightly different angles of average value 111° , *i.e.*, nearly the tetrahedral angle, with the hydrogen bonds at its ends. The angle between the plane of the benzene ring and the ZX_1 plane is 45° . Each of these six quinol molecules is connected in a

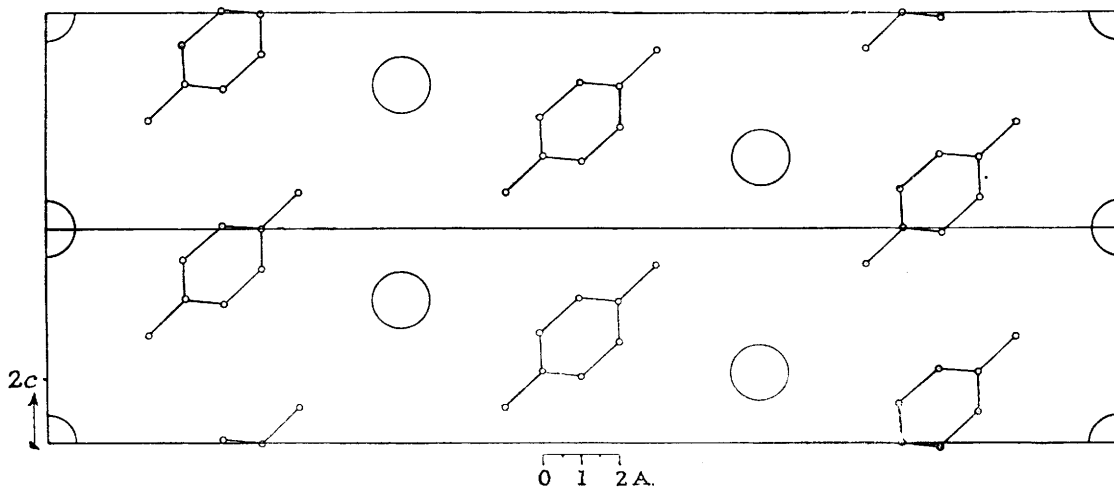
similar way through its other hydroxyl group to a separate oxygen hexagon parallel to but above or below the first. Continuation of this pattern of linkages produces an indefinitely extended set of linked cages of general rhombohedral shape as illustrated in the perspective drawing of Fig. 13. This is a very open structure. Comparison with the 2.75 Å. sides of the hexagons

FIG. 11.



Projection of the quinol molecules on the *c* face. Large open circles represent the positions of the sulphur dioxide molecules.

FIG. 12.

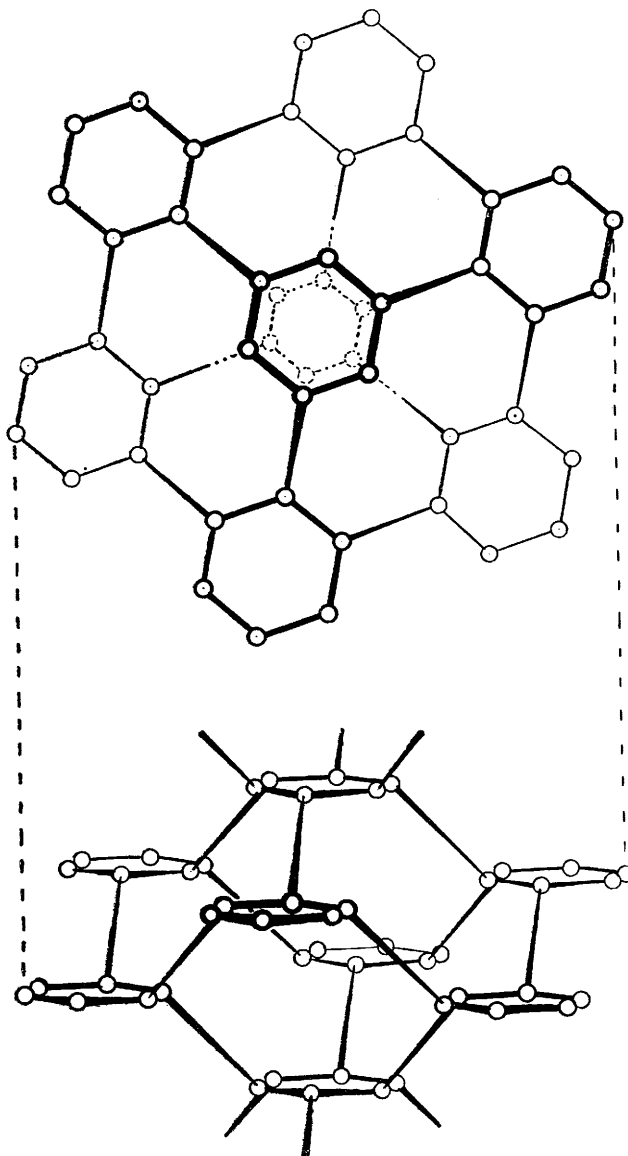


Projection of the row of molecules along the larger diagonal of Fig. 11 in plane through this diagonal and perpendicular to the *c* face.

shows a very large central space which is occupied to only an insignificant extent by the atoms of the benzene ring hexagons of side *ca.* 1.4 Å. that should be imagined on each of the sloping lines representing the O . . . O axis of one molecule. There are gaps on each face of the cage and these are so large that it is possible to insert a second identical framework structure. This is displaced vertically half-way between the top and bottom oxygen hexagons of Fig. 13, and the two frameworks make a multiple interpenetration without any closer approach of the two

independent but inseparable giant molecules than that usual for unlinked atoms. Owing to the difficulty of representing this by a perspective drawing it is shown stereoscopically in Fig. 14. In the upper part of the figure, which elsewhere shows the interpenetration of two

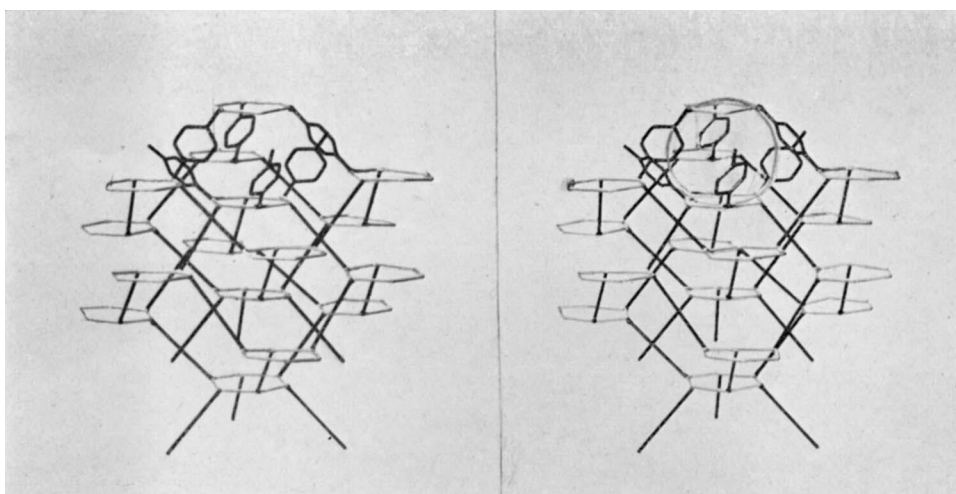
FIG. 13.



Manner of hydrogen bonding of quinol molecules. Above: In plan each regular hexagon denotes six hydrogen bonds between oxygen atoms. Hexagons at different levels are represented by different line thickness. The tapered lines, representing the O—O axis of a quinol molecule, show the method of linking to form an infinite three-dimensional cagework. Each taper points downwards from the observer. Below: Perspective drawing corresponding to above. The hexagons denote the hydrogen bonds; the longer lines connecting different hexagons denote the O—O axis of the quinol molecule.

frameworks each similar to that of Fig. 13, benzene rings have been added in the known atomic positions to show the manner of approach of the two frameworks. Although these are now separated in places at normal interatomic van der Waals distances and there are no gaps through which a molecule may easily enter or leave, there remain, between the two frameworks, cavities

FIG. 14.



Stereoscopic representation of interpenetration of two similar hydrogen-bonded cageworks each identical with that shown in Fig. 13. Benzene rings are shown by small hexagons in the upper part of the figure but are elsewhere omitted for clarity. The larger hexagons represent the hydrogen bonds. The roughly spherical space enclosed between the two cageworks is also shown.

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of sufficient size to contain a small molecule at normal unlinked distances from the surrounding atoms. Such a cavity may be seen in Fig. 14 bounded at top and bottom by oxygen hexagons of two different frameworks and at the sides by atoms of the six benzene rings shown. In this space a sphere of *ca.* $7\frac{1}{2}$ Å. diameter may be constructed to reach the centres of the enclosing atoms. After allowance for the contact radii of these atoms, this leaves a space, roughly spherical and of diameter 4 Å., in which sulphur dioxide or another small molecule may be fitted. The number of available spaces is one for every three quinol molecules. This determines the formula of the molecular compounds mentioned above. It restricts M in $3C_6H_4(OH)_2M$ to such molecules as may be fitted into the available space. The enclosed molecules, being trapped in the building-up of the structure during crystallation, are firmly retained so long as the quinol cagework remains unbroken but may escape when the cageworks are ruptured during solution, fusion, or grinding. Molecules small enough to escape from the cagework, *e.g.*, through the oxygen hexagons, will not form similar compounds.

The position of the sulphur dioxide molecules is determined from the electron-density maps. In the projection (Fig. 6) the molecule shows as a single peak of circular symmetry centred on the threefold axis. The vertical section (Fig. 9) shows, however, that the electron density computed for a section through the molecule does not have a maximum at the centre. In it two peaks are seen side by side and the general form of the peak, much elongated along the *c* axis, is what would be expected for a bent sulphur dioxide molecule rotating about an axis passing through or near the two oxygen atoms. The doubling of the sulphur peak then appears because the section is, in that neighbourhood, a cut through a roughly *torus*-shaped region of electron density produced by a sulphur atom rotating on a circle around the *c* axis. A horizontal section through the sulphur dioxide as seen in Fig. 7 gives circular contours but shows, as it should, a small decrease in electron density in the middle. Such rotations of a group of atoms in a crystal structure have been previously established in other ways, but these electron-density maps give an almost visual demonstration of the process.

The space available for rotation about a horizontal axis is restricted (see below), but it seems probable that the sulphur dioxide oxygen atoms which, if placed at $\pm 00z$ ($z = 0.217$) would be each at 3.15 Å. from the six oxygen atoms of a hydrogen-bonded OH hexagon and would act as pivots for the rotation, may undergo oscillations greater than those of the more rigidly fixed atoms of the quinol framework and in consequence do not appear as sharply resolved atoms in the vertical section through the molecule. The small deficiency in sulphur dioxide content found in analyses suggests that a number of the available holes may not be occupied. The effect of this would be to produce a lowering of the computed electron density in the regions corresponding to the sulphur dioxide.

The evidence for these vacant spaces will be considered further in a later Part dealing with other compounds of the same general formula.

It is now possible to dispose of the initial difficulties encountered in the space-group determination of this compound. The double quinol framework is itself centrosymmetric. When the spaces contain sulphur dioxide molecules, which despite their bent form are effectively centrosymmetric through rotation, the structure as a whole is centrosymmetric and has space-group $R\bar{3}$. The great similarity between X-ray results for " β -quinol" indicated an identical structure which at first was supposed to be that of the double framework with vacant spaces in place of the sulphur dioxide molecules. It was difficult to see how this could be non-centrosymmetric although the evidence for this is complete, but it was later shown (Palin and Powell, *loc. cit.*) that " β -quinol," which had previously been regarded as a polymorphic form of quinol obtained by crystallisation from methyl alcohol, is a compound of one molecule of methyl alcohol with three molecules of quinol. If the methyl alcohol molecules are placed with their lengths along the *c* axis, in positions similar to those of the sulphur dioxide molecules, but with all hydroxyl groups of the methyl alcohol molecules pointing towards the same end of the *c* axis, the structure is non-centrosymmetric if the methyl alcohol molecules cannot rotate about a horizontal axis, and has the space-group $R\bar{3}$ as required. This direct evidence of the restriction on rotation about the horizontal axis agrees with the explanation given above of the limitation of the sulphur dioxide rotation to the vertical axis.

The authors are grateful to Messrs. I.C.I. Ltd. for the opportunity given to one of them (D. E. P.) to engage in this work.