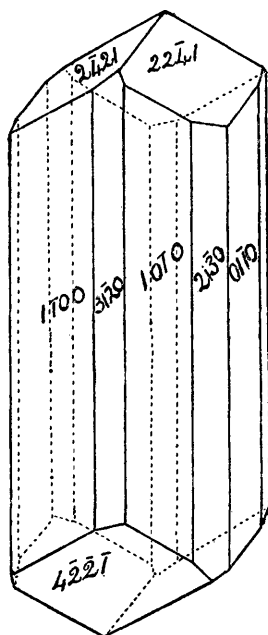


CCCXCIII.—*The Crystal Structure of Quinol. Part I.*

By WILLIAM AUGUSTUS CASPARI.

QUINOL is the only disubstituted benzene derivative except guaiacol known to crystallise in trigonal or hexagonal symmetry. Its most stable modification crystallises from water with highly acicular habit, in hexagonal prisms capped by rhombohedra. The crystals used in the present investigation (Fig. 1) were prepared by slow

FIG. 1.



evaporation, at room temperature, of aqueous solutions to which a little potassium bisulphite had been added. Prisms of all thicknesses up to 1.5 mm. were thus obtained; the prism faces in many cases showed longitudinal striations, whilst the rhombohedra usually had smooth polished faces and sharp edges.

Heydrich (*Z. Kryst. Min.*, 1910, 48, 244) placed quinol in the ditrigonal-scalenohedral or calcite class. Re-examination by the goniometer, however, showed that the hexagonal prism edges are frequently blunted by narrow faces of a third-order prism, which in some individuals may be identified on all six edges. The mean prism-zone angle between first and third orders was $40^{\circ} 58'$ (calc. for $10\bar{1}0 : 12\bar{3}0$, $40^{\circ} 54'$). The crystal must therefore be placed in the trigonal-rhombohedral or diopside class, space-group C_{3i}^1 or C_{3i}^2 . Laue photographs through the (0001) plane (which, however, was never observed as a crystal face) showed trigonal symmetry. Through the $(10\bar{1}0)$ and $(11\bar{2}0)$ planes, the latter of which, again, does not occur on the crystal, they showed no symmetry. The evidence of Laue photographs therefore confirms the above conclusion.

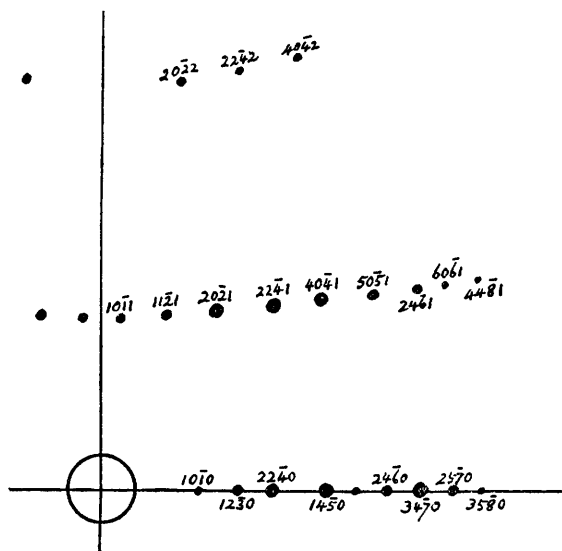
Interpenetration-twinning between right and left third-order prisms is common, and some care was needed in selecting untwinned crystals suitable for X-ray photography.

The crystal structure of quinol has been examined by Becker and Jancke (*Z. physikal. Chem.*, 1921, 99, 242), whose results are somewhat at variance with those given below. These investigators,

however, used only the powder-method, which is now known to be of minor utility for the determination of unit cells.

Crystals of the requisite quality having been secured, X-ray rotation photographs were taken with axes of rotation normal to the planes (0001), (11 $\bar{2}$ 0), and (10 $\bar{1}$ 0), respectively. A quarter of the first-named, or *c*-axis, diagram is shown in Fig. 2, the intensities of the reflexion-spots being roughly indicated by their size. From measurements of eight spots lying on two layer-lines, the cell-dimension along this axis is found to be $c = 5.62 \text{ \AA}$. The first

FIG. 2.



Quinol, rotated about *c*-axis, as for 8.0 cm. distance. $\text{Cu } K_{\alpha}$ radiation.

layer-line is rather more intense than the centre-line and much more so than the second layer-line. From this it is inferred that there is no interleaving plane of molecules normal to the *c*-axis. Oscillation photographs from the (0001) plane confirmed this conclusion: they showed a strong first-order (0001) line and (0002) and (0003) lines of diminishing intensity.

The closeness of the spots along the first layer-line in Fig. 2 indicates a long *a*-dimension of the cell; as will be seen below, its actual value is 22.08 \AA . For a hexagonal crystal, the general equation for the distances of (*hkl*) planes from an origin (compare Hull, *Physical Rev.*, 1917, 10, 661) reduces to

$$1/d^2 = 4(h^2 + k^2 + hk)/3a^2 + l^2/c^2,$$

or, for the present case,

$$1/d^2 = 0.00274(h^2 + k^2 + hk) + 0.0317l^2,$$

by means of which equation indices may be assigned to the spots as follows:

	<i>d</i> (obs.).	<i>d</i> (calc.).		<i>d</i> (obs.).	<i>d</i> (calc.).
10 $\bar{1}$ 0	9.48	9.55	10 $\bar{1}$ 1	5.47	5.39
12 $\bar{3}$ 0	7.19	7.22	11 $\bar{2}$ 1	5.11	5.01
12 $\bar{4}$ 0	5.48	5.50	20 $\bar{2}$ 1	4.75	4.84
14 $\bar{5}$ 0	4.27	4.16	22 $\bar{4}$ 1	4.03	3.94
24 $\bar{6}$ 0	3.61	3.61	40 $\bar{4}$ 1	3.60	3.60
34 $\bar{7}$ 0	3.14	3.13	50 $\bar{5}$ 1	3.16	3.15
2570	3.01	3.06	24 $\bar{6}$ 1	2.94	3.03
35 $\bar{8}$ 0	2.71	2.72	60 $\bar{6}$ 1	2.72	2.76
			4481	2.51	2.47
		<i>d</i> (obs.).		<i>d</i> (calc.).	
	20 $\bar{2}$ 2	2.63		2.69	
	22 $\bar{4}$ 2	2.55		2.51	
	40 $\bar{4}$ 2	2.40		2.42	

The rotation photographs normal to (11 $\bar{2}$ 0) and (10 $\bar{1}$ 0) determined the cell-dimension along *a* satisfactorily. The former, showing seven layer-lines, gave $a = 22.06 \text{ \AA.}$; the latter, with thirteen layer-lines, gave $a\sqrt{3} = 38.23 \text{ \AA.}$, whence $a = 22.08 \text{ \AA.}$

Both these photographs showed layer-lines of fairly even intensity, well filled with reflexion-spots. Those from the main prism presented some interest: (10 $\bar{1}$ 0) was absent, whilst (20 $\bar{2}$ 0), (40 $\bar{4}$ 0), and (60 $\bar{6}$ 0) occurred as strong spots; (50 $\bar{5}$ 0) was found only in one photograph. Taking into account the weakness of (10 $\bar{1}$ 0) on the *c*-axis photograph, we may conclude that there is a partial halving of (10 $\bar{1}$ 0); *i.e.*, these planes are interleaved half-way by a somewhat similar layer of molecules.

Oscillation-photographs from the main prism face showed five or more orders giving $d_{10\bar{1}0} = 19.1 \text{ \AA.}$ This agrees with the cell-dimension $a = 22.1 \text{ \AA.}$ if $d_{10\bar{1}0} = a\sqrt{3/2}$. It follows that the unit cell of quinol is hexagonal, not rhombohedral. That this is the case may indeed be expected from the acicular habit of the crystal, which points to much closer packing of molecules upon the prism faces than upon any pyramidal face. The space-group of the crystal is therefore C_{3i} .

On calculating the number of molecules of quinol (sp. gr. 1.33) in the cell, we find

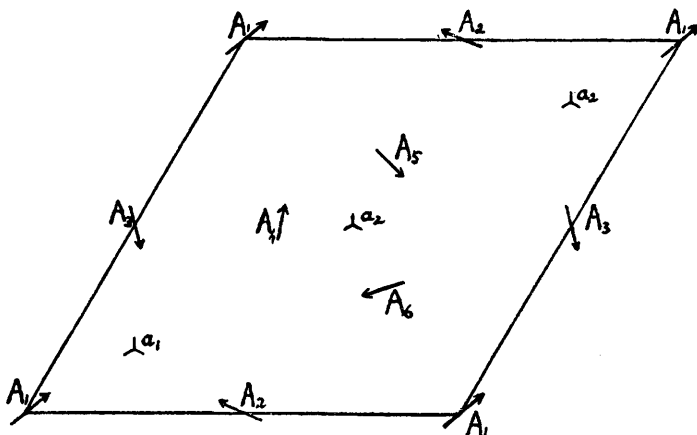
$$n = \frac{5.62 \times (22.07)^2 \times \sqrt{3/2} \times 1.33}{110 \times 1.65} = 17.4.$$

Hence there are 18 molecules to the cell. The space-group, however, requires only 6 asymmetric molecules as a maximum, and

we must infer that the lattice-units consist, not of single molecules, but of groups of three forming an asymmetric whole.

The disposition of lattice-units must be approximately as in Fig. 3, which represents a projection of the cell upon the (0001) plane. We have seen above that this plane repeats itself at 5.62 Å. intervals without interleavings. Lattice-units A_1 , A_2 , and A_3 are grouped around the triad axis a_1 . So also, but with different orientation, are A_4 , A_5 , and A_6 . Groupings around the secondary triad axes a_2 follow automatically. All the lattice-units are placed as far from one another as possible, since the space actually taken up by the molecules does not leave much room for gaps. A_2 and

FIG. 3.



Quinol, projection of unit cell upon (0001) plane. The rhombus has sides of 22.08 Å. length and is 5.62 Å. distant from the next in the plane of the paper. Each A represents a group of three molecules.

A_3 lie half-way between A_1 , in accordance with the partial halving of (10 $\bar{1}$ 0). A_6 lies on a line between A_1 and A_3 , coinciding with the developed face (12 $\bar{3}$ 0). An arrangement of the atoms cannot be attempted at present, since there is nothing to indicate how the molecules are triply associated into lattice-units.

This association of molecules found in the quinol crystal appears to have no connexion with the familiar molecular association in the liquid or gas phase. Quinol, according to Auwers (*Z. physikal. Chem.*, 1895, 18, 595), is not associated at all in naphthalene solution, and is actually less so than pyrocatechol and resorcinol, which are unassociated in the crystal. Crystal-phase association was first observed in sulphur; a recently discovered organic example is fumaric acid (Yardley, J., 1925, 127, 2207, where other examples

are cited). From unpublished results worked out by, or communicated to, the author it would appear that association of two molecules occurs in several other organic crystals, and the phenomenon may indeed be a somewhat common one.

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