CXLVII.—*The Crystal Structure of Quinol. Part II.*

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IN a previous paper (J., 1926, 2944), some account was given of the *X*-ray examination of that trigonal modification of quinol which crystallises from aqueous solutions, and may be called α-quinol. There are, however, at least two other polymorphs, one of which, here referred to as γ-quinol, is monoclinic and has been known for a long time.

β-*Modification of Quinol.*—It was found in the course of the present investigation that when quinol is deposited from methyl-alcoholic solution at the ordinary temperature, it crystallises in hexagonal

FIG. 1.

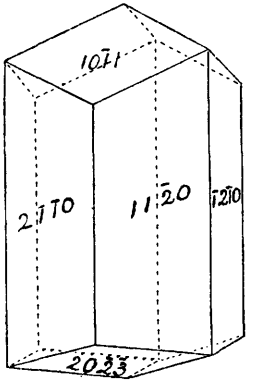
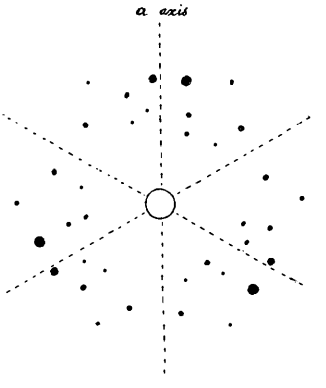


FIG. 2.



β-Quinol, Laue diagram through (0001), *as at distance* 1·75 *cm.*

prisms resembling those of α-quinol at first sight, but belonging to a different subdivision of the trigonal system. This modification may be termed β-quinol. The crystals consist of prisms capped, not by rhombohedra, but by trigonal pyramids both of the first order, with a well-marked hemimorphism along the *c* axis. The typical crystal habit is shown in Fig. 1. In general, the crystals are not so excessively acicular as those of α-quinol, the prisms tending to be fairly thick in relation to their length. The density, 1·31, and m. p., 166°, are somewhat lower than those of α-quinol.

From its external symmetry, β-quinol must be placed either in the ditrigonal-pyramidal (tourmaline) or in the trigonal-polar (sodium periodate) class. Definite evidence in favour of the latter class is afforded by Laue photographs through the (0001) plane. A diagrammatic reproduction, in which the size of the spots is an indication of their intensity, is given in Fig. 2. It will be observed that,

whilst trigonal axial symmetry about c is well brought out, symmetry about planes parallel to c is absent. The latter planes being, apart from the triad axis, the characteristic symmetry elements of the tourmaline class, β-quinol can only possess the lower symmetry of the sodium periodate class, space-groups C_3^1 to C_3^4.

Under X-ray examination, the crystals reflect considerably better than those of α- or γ-quinol. Rotation photographs about axes normal to (0001), (11$\bar{2}$0), and (10$\bar{1}$0) gave the following results:

Cell-dimension	c	(mean of	7	spots on	2	layer-lines):	c	=	5·53 Å.
„	„	a	(	„	8	„	5	„):	a	=	16·25 Å.
„	„	$a\sqrt{3}$	(	„	10	„	9	„):	$a\sqrt{3}$	=	28·12 Å.
								whence	a	=	16·24 Å.

In the c photograph the first layer-line is the strongest both in number and in intensity of spots. In all three photographs equally, (30$\bar{3}$0) and (22$\bar{4}$0) give the strongest reflexions in the prism zone, whilst among pyramidal forms (13$\bar{4}$1) and (12$\bar{3}$1) stand out by the intensity of their reflexions.

Oscillation photographs about c through 10° including the main prism face (11$\bar{2}$0) showed lines at 8·1 Å., 4·05 Å., and 2·7 Å. Since $d_{11\bar{2}0}$ is thus $a/2$, a hexagonal lattice, as in the case of α-quinol, is indicated.

For the number of molecules per cell we have

$$n = \frac{5{\cdot}53 \times (16{\cdot}25)^2 \times \sqrt{3}/2 \times 1{\cdot}31}{110 \times 1{\cdot}65} = 9{\cdot}1,$$

i.e., 9 molecules. The maximum number of lattice-units required for the symmetry of a trigonal-polar crystal is three. Consequently each unit contains the substance of three molecules, three such units going to the cell. The three molecules in each unit have no symmetry, either in each molecule separately or in the three as a group. We have here, then, another such case of triple crystallographic association as in α-quinol (*loc. cit.*). In the present instance, three of the composite lattice-units are arranged about triad axes of symmetry throughout the crystal; but neither the lattice-units nor their orientations in the cell provide a plane of symmetry normal to the c axis. The space-group of β-quinol, finally, appears to be C_3^1.

γ-Modification of Quinol.—When quinol is crystallised by sublimation, a small proportion of the mainly acicular sublimate takes the form of thin leaflets having the contours of an acute-angled rhomb. Lehmann (*Z. Kryst. Min.*, 1877, **1**, 43) found this polymorph, or γ-quinol, to be monoclinic-prismatic, with $\beta = 107°$, the flat face being (001) and the prism contours {11$\bar{1}$}. The present X-ray results entirely confirm this interpretation.

In density, 1·325, and m. p., 169°, the crystal resembles α-quinol

rather than β-quinol. The leaflets frequently undergo spontaneous distortion within a few hours of being prepared, and gradually become opaque in the course of a few weeks; hence this modification of quinol does not appear to be stable at the ordinary temperature.

Rotation-photographs about the axes set up by Lehmann provided the following data :

Cell-dimension along	a	(mean of	6	spots on	4	layer-lines) :	a =	13·24 Å.
,, ,,	b	(,,	5	,,	2	,,) :	b =	5·20 Å.
,, ,,	c	(,,	6	,,	3	,,) :	c =	8·11 Å.

The number of molecules per cell is given by

$$n = \frac{13{\cdot}24 \times 5{\cdot}20 \times 8{\cdot}11 \times \sin 73° \times 1{\cdot}325}{110 \times 1{\cdot}65} = 3{\cdot}95,$$

i.e., 4 molecules. In the rotation photographs, the strongest reflexion was from (002), with weaker ones from (004) and (006), and none from odd orders of the base. Reflexions of more than average intensity were also given by (001), (012), and (200). No halvings of (*hkl*) planes could be traced, but (010) is halved, and (*hol*) planes in which either h or l is odd. It may be inferred, therefore, that the γ-quinol crystal falls into space-group C_{2h}^5, and is built up on the simple lattice Γm.

The proximate data for the crystal structure of quinol are thus at hand, and further methods of investigation will lead to an understanding of the arrangement of atoms and molecules in the several crystals. It is seen that although quinol, like most organic substances, can crystallise in unimolecular units and monoclinic symmetry (γ-quinol), yet it tends in its stabler forms (α- and β-quinol) to associate in termolecular units and to crystallise in the trigonal system. In its trigonal modifications, quinol, like the trigonal crystals quartz (Bragg and Gibbs, *Proc. Roy. Soc.*, 1925, *A*, **109**, 405) and carborundum (Ott, *Z. Krist.*, 1926, **63**, 1), shows a tendency to preserve certain simple axial relations in its passage from one polymorph to another. Thus the c axes of α- and β-quinol are almost the same, whilst the respective a axes are nearly in the ratio of 4 to 3. The better reflecting power of the planes in β-quinol than of those in α- and γ-quinol is another datum which, although its exact bearing is not clear at present, must play its part in the ultimate interpretation of these crystals.

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