LXXIX.—*The Crystal Structure of Catechol.*

By William Augustus Caspari.

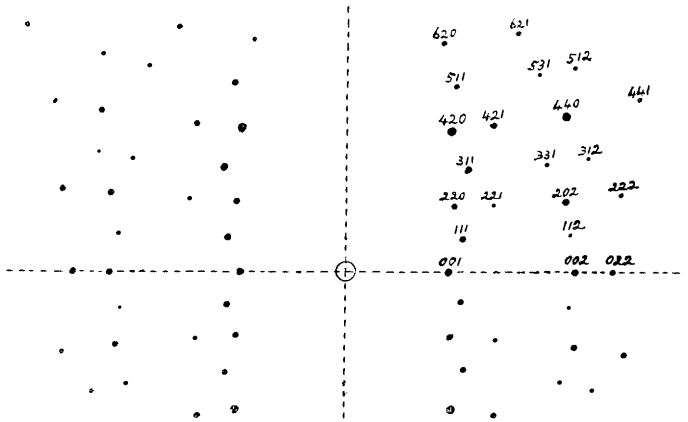
The crystal morphology of catechol is known from the measurements of Beckenkamp (*Z. Kryst. Min.*, 1900, **33**, 599), who assigned catechol to the monoclinic-prismatic class, axial ratios

1·6086 : 1 : 1·0229, $\beta = 94°15'$. In the present investigation, the rotating-crystal method has been used, and has led to definite data for the crystal cell and the space-group of catechol.

Perfectly developed crystals were obtained without difficulty by the slow evaporation of an aqueous solution. They were in most cases bounded by the three pinacoids; occasionally the prism {110} also appeared; swallow-tail twins about {100} were observed in a few instances.

X-Ray photographs were taken on glass plates through crystals set with the three crystallographic axes as rotation axes. The apparatus was of a simple character with a pinhole beam and requires no description; a Shearer tube with copper anticathode was used.

FIG. 1.



Catechol. Rotation axis a.

Figs. 1, 2, and 3 show the diagrams obtained by projecting the photographs on paper and marking the spots. As a rough guide to intensity, the size of the spots has been proportioned to the intensity of the photographic spots as far as possible. Spots due to $K\beta$ radiation are omitted. The scale of the diagrams corresponds to a distance of 4·8 cm. between the plate and the crystal.

The dimensions of the unit cell follow directly from these photographs. Each spot represents the reflexion from a definite crystal plane, and the spots arrange themselves in layer lines upon which all planes have one index in common; these lines in the case of a flat plate take the form of hyperbolas. The spacing corresponding to the distance of the apex of the first hyperbola from the straight centre line is the length of the unit cell along the axis in question,

and those of further hyperbolas are consecutive multiples. Calculations are based on the formula

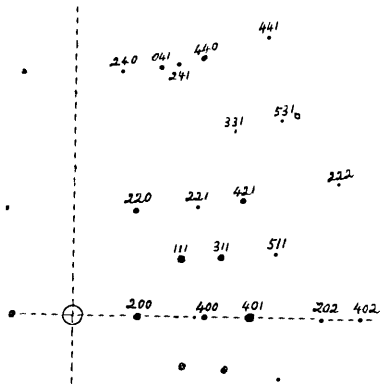
$$a(\text{or } b \text{ or } c) = n \times 1{\cdot}54 \,/\cos \mu \text{ Å.},$$

where n is the series number of the layer line, and 1·54 Å. the wavelength of copper $K\alpha$ radiation. The following cell dimensions were thus obtained :

along a axis, mean of 5 layer lines, $a = 17{\cdot}46$ Å.
,, b ,, ,, 4 ,, ,, $b = 10{\cdot}74$ Å.
,, c ,, ,, 2 ,, ,, $c = 5{\cdot}48$ Å.

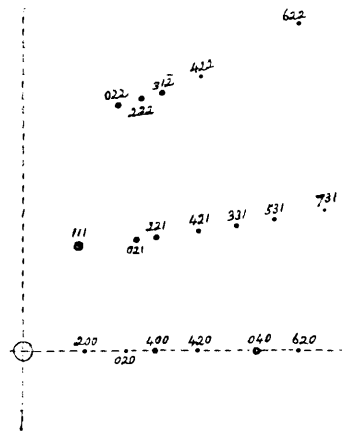
The ratios of these dimensions, *viz.*, 1·62 : 1 : 0·51, agree with the goniometric axial ratios except that c has been stated at double its

FIG. 2.



Catechol. Rotation axis b.

FIG. 3.



Catechol. Rotation axis c.

proper length by Beckenkamp. The axial ratios of catechol should be written 1·6086 : 1 : 0·5114.

To find the number of molecules in the unit cell, we have as the weight of the cell, the density of catechol being 1·375,

$$17{\cdot}46 \times 10{\cdot}74 \times 5{\cdot}48 \times \sin 94°15' \times 1{\cdot}375 = 1403 \times 10^{-24} \text{ g.}$$

The weight of the molecule being $110 \times 1{\cdot}65 \times 10^{-24}$ g., the quotient is 7·8. That is, there are eight molecules in the unit cell. Indices can now be assigned to the various photographic spots by calculating the spacing d of each and applying the stereometric formula proper to the monoclinic system, which in the present case takes the form

$$1/d^2 = 0{\cdot}0033h^2 + 0{\cdot}0087k^2 + 0{\cdot}0331l^2 - 0{\cdot}0016hl.$$

The indices of all the planes observed are tabulated below.

Rotation Axis a.			*Rotation Axis* b.			*Rotation Axis* c.		
Plane.	*d* obs.	*d* calc.	Plane.	*d* obs.	*d* calc.	Plane.	*d* obs.	*d* calc.
{001}	5·44	5·49	{200}	8·81	8·70	{200}	8·67	8·70
{002}	2·71	2·75	{400}	4·42	4·35	{020}	5·39	5·36
{022}	2·41	2·45	{401}	3·46	3·54	{400}	4·34	4·35
{111}	4·73	4·79	{202}	2·67	2·68	{420}	3·32	3·38
{112}	2·69	2·66	{402}	2·36	2·41	{040}	2·67	2·68
{220}	4·58	4·56	{111}	4·73	4·79	{620}	2·49	2·55
{221}	3·58	3·58	{311}	3·76	3·88	{111}	4·75	4·79
{202}	2·62	2·68	{511}	2·86	2·93	{021}	3·80	3·84
{222}	2·34	2·39	{220}	4·52	4·56	{221}	3·63	3·58
{311}	3·76	3·88	{221}	3·55	3·58	{421}	2·92	2·96
{331}	2·68	2·70	{421}	2·96	2·96	{331}	2·56	2·70
{312}	2·44	2·50	{222}	2·31	2·39	{531}	2·33	2·31
{420}	3·38	3·38	{331}	2·64	2·70	{731}	2·05	2·07
{421}	2·94	2·96	{531}	2·33	2·31	{022}	2·44	2·45
{440}	2·30	2·28	{240}	2·53	2·56	{222}	2·32	2·39
{441}	2·12	2·14	{041}	2·42	2·41	{31$\bar{2}$}	2·27	2·34
{511}	2·88	2·93	{241}	2·33	2·34	{422}	2·15	2·20
{531}	2·35	2·31	{440}	2·28	2·28	{622}	1·91	1·94
{512}	2·12	2·19	{441}	2·11	2·14			
{620}	2·55	2·55						
{621}	2·27	2·38						

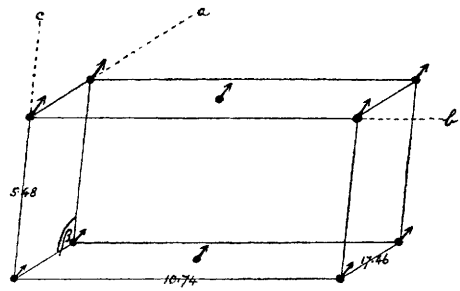


FIG. 4.

The table shows that in all cases the sum of the indices h and k is an even number, and that there are no other regularities connecting the various indices. From this it follows that if the cell be represented by four equal molecules at the corners of a parallelipiped, there must be molecules of the same orientation in the centres of the {001} faces (Fig. 4). Hence the space-lattice is Γ_m' and, further, the space-group is narrowed down to C_{2h}^3. For this space-group, eight asymmetric molecules is the full number permissible; the catechol molecule, therefore, is without any intrinsic symmetry in the crystalline state. Each primary molecule, as shown in Fig. 4, must have three other differently oriented molecules near it.

As regards the actual disposition of the molecules in the crystal, we have as arguments the above symmetry data, the crystal

habit, and the size and shape of the catechol molecule. The evidence at hand points to a simple parallelipipedic arrangement, such that all the molecules are as it were skewered along the *b* axis, with the plane of the benzene rings lying parallel to *a* and *c* and the hydroxyl groups pointing pairwise alternately backward and forward along the *a* axis. Detailed discussion may, however, be deferred pending the examination of 2 : 3-dihydroxynaphthalene and 2 : 3-dihydroxyanthracene, which is now in progress. The above arrangement is in harmony with the reticular densities of the crystal faces; these would work out as follows :

{100}	face,	1 molecule in	14·7 Å^2.
{001}	,,	,,	23·5 ,,
{010}	,,	,,	48·0 ,,
{110}	,,	,,	57·0 ,,

In the majority of the crystals, {100} is decidedly the most developed and {010} the least developed face, whilst {110} occurs only sporadically; the order of the reticular densities is thus the same.

The author desires to express his indebtedness to Sir William Bragg, F.R.S., and to his fellow-workers at the Davy Faraday Laboratory for the helpful interest taken by them in this investigation; also to the authorities of the Royal Institution for apparatus and laboratory facilities.

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