ON THE CRYSTAL STRUCTURE OF PHTHALIMIDE. PART I.—DETERMINATION OF THE SPACE-GROUP

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(Plate V)

ABSTRACT. Single crystals of phthalimide were studied goniometrically and with X-rays. Goniometric data assign it to the monoclinic holodedral class in agreement with Groth.

The axial ratios, obtained from X-ray studies, are a:b:c = 2.98:1:0.4946. Phthalmide is found to belong to space group C^5_{2h}—$P2_1/n$.

According to Groth (1906) phthalimide crystallises in the monoclinic holohedral class with axial ratios $a : b : c = 1.4913 : 1 : 0.4967$ and $\beta = 91°18\frac{3}{4}'$.

The X-ray data of this substance is completely lacking. The present paper deals with the determination of the axial lengths and the space-group of phthalimide.

PREPARATION OF THE CRYSTAL

It is very difficult to get perfect single crystals of phthalimide. Several attempts were made to crystallise it from a solution of alcohol, alcohol and acetic acid, acetic acid and ethyl acetate. None of the solvents had been found to be highly satisfactory. However, amongst the solvents tried, ethyl acetate was found to be the best medium for crystallisation. After repeated and careful crystallisations, only a few perfect single crystals were obtained.

The crystals were all needle-shaped. They were studied with the help of the Czapski Theodolite two-circle goniometer. The observed angles between the various faces were found to agree with those reported by Groth (*loc. cit.*).

MEASUREMENT OF AXIAL LENGTHS

Hadding-Siegbahn type of x-ray tube with copper anticathode was used. Rotation photographs were taken with a cylindrical camera.

(*i*) Rotation about *c*-axis:

The *c*-axis being the long axis of the crystal itself can be easily set by making the prism faces vertical. The photograph is shown in Plate V Fig. 1 and the mean axial length measured from the different layer lines given by Cu K_α and Cu K_β is found to be $c = 3.765$ Å.

(*ii*) Rotation about *b*-axis :

The *b* (010) face does not develop in the crystal. The *b*-axis becomes vertical when the reflections from the prism faces lie in the vertical plane and the bisector between *m* (110) and *m'* ($\bar{1}10$) becomes vertical.

The mean axial length, $b = 7.611$ Å, is found from the rotation photograph (Fig. 2).

(*iii*) Rotation about *a*-axis :

Both *b* (010) and *c* (00$\bar{1}$) faces being absent, *a*-axis was fixed by setting *q* (011) and $\bar{q}'$ (01$\bar{1}$) faces vertically.

The rotation photograph (Fig. 3) gives the mean value $a = 22.70$ Å.

Thus the axial ratios, given by the x-ray studies of the crystal are found to be

$$a : b : c = 2.98 : 1 : 0.4946.$$

Comparing the results with those given by Groth (*loc. cit.*) it is found that the length of the *a*-axis is twice the value assumed by Groth.

In order to determine correctly the space-lattice and the space-group the reflecting spots must be identified and indexed unambiguously.

DETERMINATION OF THE SPACE-LATTICE

Oscillation photograph :

The crystal was set with the *c*-axis vertical. The oscillation started with the incident beam normal to a (100) face, *i.e.*, parallel to the reciprocal a-vector -a*-axis. The ocillation ranging from 0° – 180° was covered in ten successive stages, each oscillating within the range of 18°.

The theoretical Bragg angle of reflection of diffracted planes which alone can appear in the oscillation picture as judged from the reciprocal lattice are compared with those obtained from the direct measurement of the photograph. Thus every spot in the photograph is accounted for and given the proper index. The theoretical angles are calculated from the equation

$$\text{Sin}\ \theta = \frac{\lambda}{\sin\beta}\sqrt{\left[\left(\frac{h}{a}\right)^2 + \left(\frac{k\sin\beta}{b}\right)^2 + \left(\frac{l}{c}\right)^2 - \frac{2hl}{ac}\cos\beta\right]}$$

where θ is the Bragg angle of reflection of the plane (*hkl*).

a, *b*, *c* are the axial lengths already determined

β is the axial angle determined from goniometric studies.

A perusal of the indices of the planes reflected in the central layer line showed that no special conditions guide the reflection of (*hko*) planes.

Since there is no restriction in the appearance of (*hko*) reflections, there cannot be also any systematic absent spectra in the general (*hkl*) reflections. Hence, being superfluous, higher layer lines of the *c*-axis oscillation photographs were not analysed.

The unit cell of phthalimide, therefore, belongs to the simple monoclinic lattice.

DETERMINATION OF THE SPACE-GROUP

Weissenberg photographs :

One of the axes being too long, the angles of reflection of (*oko*) planes lie very close to that for (*lko*). Hence in order to decide unambiguously the nature

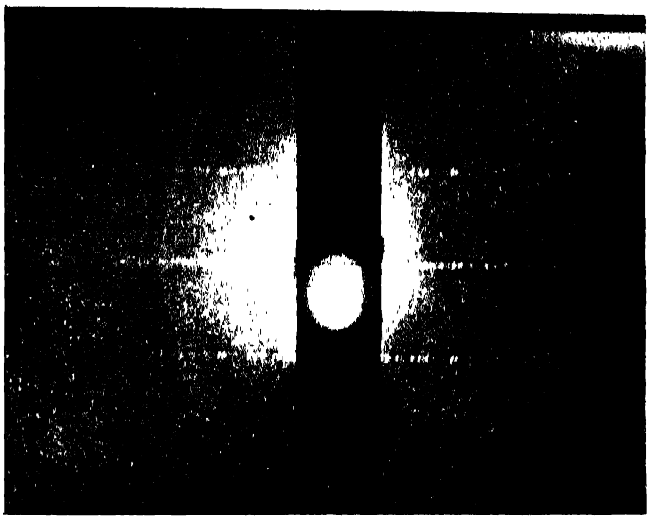

Fig. 1
Rotation photograph
about *c*-axis

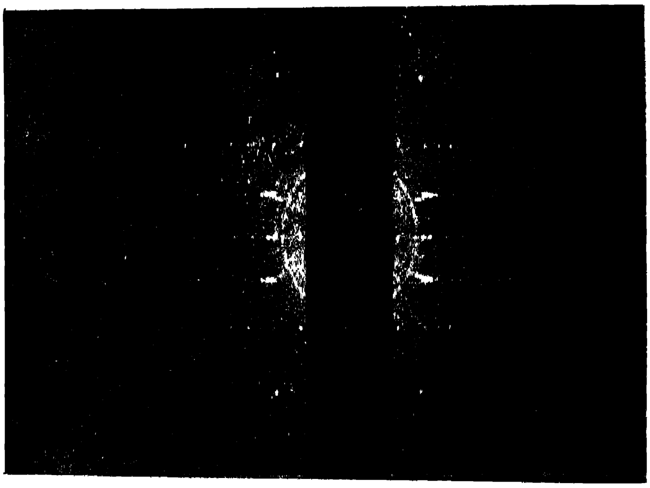

Fig. 2
Rotation photograph
about *b*-axis.

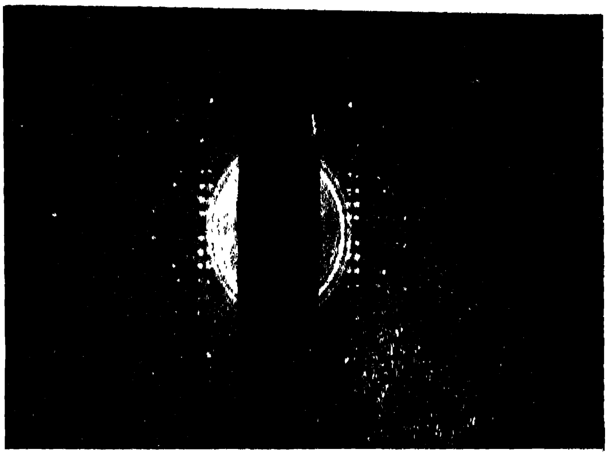

Fig. 3
Rotation photograph
about *a*-axis.

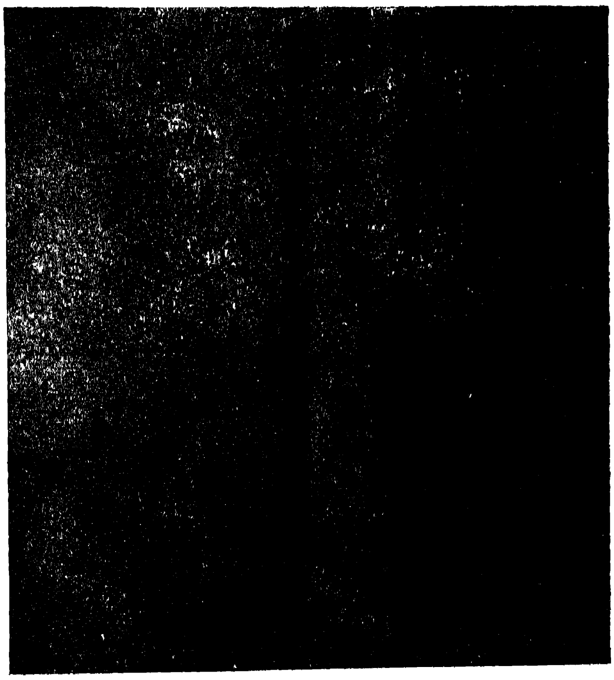

Fig. 4
Rotation photograph
about *c*-axis.

of (*oko*) reflections, Weissenberg photograph of the central layer line around *c*-axis of the crystal was taken (Fig. 4).

All the spots were correctly indexed. It was found that no systematic absent spectra occur in the reflection of (*hko*) planes, as already indicated by oscillation photographs, but (*hoo*) and (*oko*) reflections occur only when *h* and *k* are even.

Since the crystal belongs to the monoclinic hololedral class, halving of (*oko*) indicates a two fold screw axis along *b* while halving of (*hoo*) indicates a glide-plane of symmetry normal to the *b*-axis and having a glide of $a/2$ or $(a+c)/2$.

To choose between these two alternatives we have to study the nature of (*hol*) reflections.

For this purpose a Weissenberg photograph of the central layer line around *b*-axis of the crystal was taken. This also gives us directly the angle β between *a*-and *c*-axes.

β was found to agree satisfactorily with the value reported by Groth.

Indices of all the spots showed that not only the odd orders of (*hoo*) and (*ool*) are absent but also all reflections from (*hol*) where $(h+l)$ is odd, are absent. This means that the glide is $(a+c)/2$ and not $a/2$.

As all the necessary and requisite conditions of finding out the correct space-group of a monoclinic lattice (*cf.* Astbury and Yardley) have been determined, the nature of (*o k l*) reflections were not studied.

To sum up, it is found that (*i*) *b*-axis is a two-fold screw axis, since odd orders of (*o k o*) reflections are absent and (*ii*) the plane normal to the *b*-axis, *i.e.*, (010) plane is a glide plane of symmetry with a glide of $(a+c)/2$, since all reflections from (*hol*) where $(h+l)$ is odd are absent.

On comparing these criteria with those given by Astbury and Yardley (*loc. cit.*) the space-group is found to be $C^5_{2h}-P2_1/n$

NUMBER OF MOLECULES IN THE UNIT CELL

The number of molecules per unit cell, *n*, is given by the relation

$$\rho = n.\ M.\ m/V$$

where ρ = density of the phthalimide crystal.

n = the number of molecules of phthalimide $C_6H_4(CO)_2NH$ per unit cell.

m = wt. of H atom = 1.649×10^{-24} gm.

M = molecular weight of phthalimide = 147.

V = volume of the unit cell

$= abc \text{ Sin } \beta$

$= 22.7\times7.611\times3.765\times\text{Sin } 91^\circ 18\tfrac{2}{3}'\times10^{-24}$ c.c.

$= 6.504\times10^{-22}$ c.c.

The density was determined by the flotation method from a solution of zinc sulphate. It was found to be 1.452

Hence the number of molecules, *n*, per unit cell

$$\rho V/Mm = 3.896 \approx 4.0.$$

SUMMARY

The axial lengths *a*, *b* and *c* were found out from the three rotation photographs. The length of the *a*-axis is found to be twice that assumed by Groth.

The axial ratios are $a : b : c = 2.98 : 1 : 0.4946$.

Oscillation photographs around *c*-axis showed the general nature of (*hko*) and (*hkl*) reflections indicating the presence of the simple lattice.

Zero-layer-line Weissenberg photographs around *b* and *c*-axes were taken. The *b*-axis photograph gave β angle agreeing fairly well with that found optically, *viz.*, $91°18\frac{2}{3}'$.

All reflections from (*hol*) planes where $(h+l)$ is odd are absent.

From *c*-axis photograph it was found that all odd orders of (*oko*) reflections are absent.

Hence *b*-axis is a two-fold screw axis and (*ac*)-plane is a glide plane of symmetry with a glide $(a+c)/2$, and the space-group is $C^5_{2h} - P2_1/n$

$$a = 22.700 \text{ Å}$$
$$b = 7.611 \text{ Å}$$
$$c = 3.765 \text{ Å}$$
$$\beta = 91^\circ\ 18\tfrac{2}{3}'$$
$$n = 4.$$

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