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The Crystal Structure of Ortho-Iodobenzoic Acid

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x-Ray analysis of organic crystals usually leads no farther than to the determination of a possible unit cell and the space group. Occasionally it is possible to probe a bit more deeply into the arrangement in the cell. In these cases the results are of interest for stereochemical considerations of the molecule and the molecular arrangement within the cell. It seems worth while at this time to report the results of the study of *o*-iodobenzoic acid, which has led to the determination of the positions of the iodine atoms in the cell.

Groth[1] gives the following data for this monoclinic crystal: $a:b:c$ = 0.7964:1:0.2880, β = 110° 28.5′; m. p. 161°; sp. gr. 2.249. The material used in this investigation was Eastman Kodak Company chemically pure product further purified by two vacuum sublimations. The resulting product was colorless and melted at 161.6–162.0°. The crystals used were grown from ether or from a mixture of equal parts of ethyl and isoamyl acetates. These were needles along the *c* axis with the prism faces (110) developed. Small end faces (011) and (101) were also present. The structure analysis was made by means of powder, Laue and oscillation photographs.

The Unit of Structure.—Powder photographs[2] were taken with Mo K_α radiation, using sodium chloride as a standard. These were analyzed by the usual methods, and required a 4-molecule cell to account for all the lines.

Laue photographs[2] were taken with the incident beam of x-rays nearly perpendicular to (010), (110), and inclined at an angle of approximately 20° to the normal to (110). The short wave length limit of the incident beam (from a tungsten target) was 0.31 Å. The assumption of a 4-molecule cell gave $n\lambda$ values down to 0.31 Å. but not below. As in the case of *m*-iodobenzoic acid,[3] the strongly absorbing iodine absorbed all wave lengths between its critical absorption limit 0.37 Å., and the short wave length limit, 0.31 Å., except in the case of a very few spots. Thus most of the first-order spots had an $n\lambda$ value between 0.37 Å. and 0.48 Å.

Oscillation photographs were taken with Mo K_α radiation using a cylindrical film, the crystal being oscillated through 15° about a crystallographic axis in each case. These were indexed by Bernal's graphic method,[4] and the fundamental translations of the unit cell were calculated by the

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(1) Groth, "Chemische Kristallographie," Engelmann, Leipzig, 1906, Vol. IV, p. 465.

(2) These photographs were taken at Ohio State University, Columbus, Ohio, in 1926–1927 while the author was a graduate student there.

(3) Klug, Mack and Blake, THIS JOURNAL, **51**, 2882 (1929).

(4) Bernal, *Proc. Roy. Soc.* (London), **A113**, 117 (1927).

Polanyi formula from careful measurements of the layer lines. The dimensions of the unit cell are

$$a_0 = 11.71 \text{ Å}. \quad b_0 = 15.17 \text{ Å}. \quad c_0 = 4.336 \text{ Å}. \quad \beta = 110^\circ\, 28.5'$$

The axial ratios calculated from these data are $a{:}b{:}c = 0.7719{:}1{:}0.2863$, in good agreement with the crystallographer's values above.

The Laue photograph with the incident beam perpendicular to (010) showed two pseudo planes of symmetry almost at right angles to each other. Because of this pseudo-orthorhombic nature a more desirable cell can be formed by making the short diagonal of the projection of (010), based on Groth's axial ratios, the (001) of a new cell. The dimensions of the new 4-molecule cell are (calculated from x-ray data)

$$a_0 = 11.30 \text{ Å}. \quad b_0 = 15.17 \text{ Å}. \quad c_0 = 4.336 \text{ Å}. \quad \beta = 90^\circ\, 43'\, 47''$$

These lead to the new axial ratios $a{:}b{:}c = 0.7450{:}1{:}0.2863$ with $\beta = 90^\circ\ 43'\ 47''$. Oscillation photograph No. 5 about Groth's *a* axis confirmed the desirability of the new choice of cell. It is also in keeping with the crystallographic custom of choosing the axes so as to make angle β as nearly 90° as possible. The end faces on the crystal designated (101) and (011) by Groth now become (001) and ($\bar{1}11$), respectively, with the new set of axes. All photographs were analyzed on the basis of the new axes, and all indices in this paper refer to the cell based on these axes.

The Space Group.—The space group determination was based on the data from the Laue photographs. Since first-order Laue reflections were observed from all types of pyramidal planes the space group is based on the simple monoclinic lattice Γ_m. All types of prism planes were found to be present in the first-order (Table I) except ($h0l$) when h is odd, and ($0kl$) when k is odd. The latter has no significance from a space group standpoint in the monoclinic system, but indicates a pseudo-glide plane parallel to (100) with a translation of $b/2$. Actually the reflections (011), (031) and

TABLE I

FIRST-ORDER PRISM REFLECTIONS ON LAUE PHOTOGRAPHS

Photograph No. 2				Photograph No. 3			
Planes reflecting		Planes not reflecting		Planes reflecting		Planes not reflecting	
(hkl)	$n\lambda$	(hkl)	$n\lambda$	(hkl)	$n\lambda$	(hkl)	$n\lambda$
405	0.45	$10\bar{2}$	0.46	$20\bar{3}$	0.55[a]	504	0.39
$20\bar{3}$	.44	103	.40	403	.55[a]	704	.49
023	.43	304	.53[a]	$06\bar{5}$	.52[a]	$50\bar{4}$	.58[a]
$04\bar{3}$	.46	$30\bar{4}$	.37	$4\bar{3}0$	.48	$30\bar{4}$	.44
$\bar{7}90$	.39	305	.37	$7\bar{5}0$	.34	$70\bar{5}$	.48
$\bar{5}70$	.39	506	.39	$8\bar{5}0$	.44	$70\bar{6}$	.38
$\bar{3}70$	.42			$\bar{5}60$	.41		
$\bar{9}.10.0$	.46			$17.\bar{7}.0$	.38		
$\bar{4}.11.0$	.44			$17.\bar{5}.0$	.48		
$\bar{5}.16.0$	.40						

[a] The short wave length limit in the case of these photographs was known to be at 0.31 Å.

(032) were observed on oscillation photographs, showing that the approximation to an arrangement requiring (0*kl*) absent when *k* is odd, while close, is not complete. Since all of the (*h*0*l*) planes with *h* odd listed in Table I were in a position to reflect in the first order on some one of the Laue photographs, but failed to, their absence has been assumed to be a legitimate space group absence.

One other absence occurs on oscillation photograph No. 2. All odd orders of (0*k*0) are absent, while (020), (040), (060) and (080) are present. The only monoclinic space group requiring the observed absences is C_{2h}^5 which, therefore, has been accepted as the correct one. All data from the various types of photographs are in agreement with this choice.

Atomic and Molecular Arrangement in the Cell.—For small orders of reflection in the case of a compound like *o*-iodobenzoic acid, the benzene rings no doubt contribute very little to the intensities because of their large self-interference. Thus the intensities observed are due largely to the scattering of the heavy iodine atoms which make up more than half the weight of the molecules. By neglecting the carbon, hydrogen and oxygen atoms, and assuming the intensities to be due entirely to the iodine atoms, it is possible to locate the positions of the iodine atoms reasonably accurately.

In space group C_{2h}^5 the four iodine atoms could all be equivalent, or they might be divided into two sets of two equivalent atoms. The latter case places the iodine atoms in centers of symmetry. The observation on oscillation photograph No. 3 of (400) > (200) rules this out. It is also chemically improbable that the iodine atoms would occupy these centers of symmetry. The iodine atoms are located, therefore, in the four general positions. Wyckoff's[5] coördinates for these positions (interchanging his *b* and *c* indices to make the coördinates agree with the choice of axes used in this paper) are

$$xyz;\ \tfrac{1}{2} - x,\ y + \tfrac{1}{2},\ \bar{z};\ x + \tfrac{1}{2},\ \tfrac{1}{2} - y,\ z;\ \bar{x}\bar{y}\bar{z}$$

The oscillation photographs furnish data for evaluating these parameters with fair accuracy.

In this case, neglecting extinction, a quantity proportional to the integrated intensity of reflection of the Mo K_α line from a plane (*hkl*) is S^2, where

$$S = \left(\frac{1 + \cos^2 2\Theta}{2 \sin 2\Theta}\right)^{1/2} \sum_n f_n e^{2\pi i(hx_n + ky_n + lz_n)}$$

in which f_n is the usual atomic scattering factor for the n^{th} atom. The f value for iodine used in this paper was obtained from Pauling and Sherman's recent paper.[6] Approximate values for each of the parameters were determined from the appropriate set of pinacoid reflections by cal-

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[5] Wyckoff, "The Analytical Expression of the Results of the Theory of Space-Groups," Carnegie Institution Publication No. 318, Washington, 1922, p. 51.

[6] Pauling and Sherman, *Z. Krist.*, **81**, 27 (1932).

culating S^2 values and comparing them with the observed intensities visually estimated. The curves in Fig. 1 show that the observed intensities, (400) > (200) > (600) > (800), (060) > (020) $\equiv$ (040) > (080), and (001) > (002) > (003), are approximately satisfied by the following

$$x = 0.10,\ 0.15,\ 0.35 \text{ or } 0.40$$
$$y = 0.09,\ 0.16,\ 0.34 \text{ or } 0.41$$
$$z = 0.00 \pm 0.05 \text{ or } 0.50 \pm 0.05$$

The various combinations of the above parameters narrow down to four non-identical cases to be considered:

1. $x = 0.10$ $y = 0.09$ $z = 0.00 \pm 0.05$
2. $x = 0.10$ $y = 0.16$ $z = 0.00 \pm 0.05$
3. $x = 0.15$ $y = 0.09$ $z = 0.00 \pm 0.05$
4. $x = 0.15$ $y = 0.16$ $z = 0.00 \pm 0.05$

To determine the correct set of x and y parameters, values of S^2 for a set of $(hk0)$ planes were calculated for the four combinations above, and for small deviations from the values listed in the combinations, and compared with the observed intensities (Table II). The best values were found to be $x = 0.14$ and $y = 0.08$. The value for z was found to be close

TABLE II

INTENSITY DATA FROM PINACOID AND PRISM REFLECTIONS ON OSCILLATION PHOTOGRAPHS

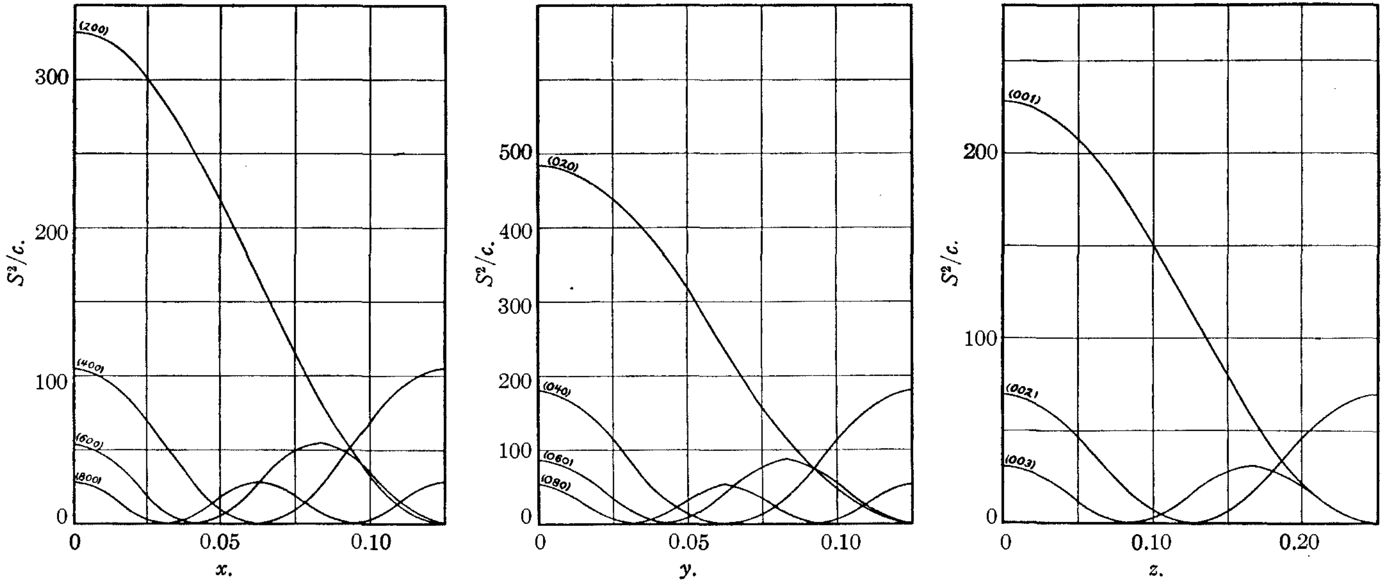
(S^2 based on the final parameter values; $x = 0.14$, $y = 0.08$ and $z = 0.02$)

Pinacoid Reflections

Photograph No. 2			Photograph No. 3			Photograph No. 4		
(hkl)	I	$S^2/5000$	(hkl)	I	$S^2/5000$	(hkl)	I	$S^2/15000$
020	6	11.0	200	5	5	001	6	13
040	6	3.0	400	8	20	002	4	4
060	8	8.5	600	4	6	003	2	2
080	3	2.0	800	2	2			

Prism Reflections

A. $(hk0)$ Photo. No. 3			B. $(0kl)$ Photo. No. 4			C. $(h0l)$ Photo. No. 3		
(hkl)	I	$S^2/5000$	(hkl)	I	$S^2/5000$	(hkl)	I	$S^2/5000$
310	8	19.8	011	5	0.2	$\bar{2}01$	2	0.1
420	5	4.6	021	9	10.2	$\bar{4}01$	7	14.7
510	1	1.0	022	3	3.5	$\bar{6}01$	3	1.6
520	5	8.8	023	4	1.5	$\bar{8}01$	1	3.4
620	1	0.8	031	$^1/_2$	0.4	201	7	3.0
630	5	6.6	032	$^1/_{10}$	0.7	401	7	12.2
720	1	0.1	041	2	3.8	601	5	3.7
730	1	.03	042	6	1.8	801	2	2.1
740	1	.1						
750	1	3.7						
830	2	2.4						
840	1	0.5						
850	2	.7						
860	2	2.2						
940	1	3.0						



Crystal structure of ortho-iodobenzoic acid. Crystal structure of ortho-iodobenzoic acid. Crystal structure of ortho-iodobenzoic acid.

Fig. 1.—Structure factor curves for the various pinacoid reflections for ranges of values of the parameters leading to non-identical structures.

to 0.02 by calculating values of S^2 for sets of ($h0l$) and ($0kl$) planes and comparing with observed intensities (Table II).

It must be remembered that complete agreement is not to be expected between the calculated and observed intensities in this analysis, since the effect of the carbon and oxygen atoms has been neglected entirely. Inasmuch as a change of a very few hundredths in the values of the parameters destroys the qualitative agreement, the results may be accepted with considerable faith.

Figure 2-A is a projection on (001) parallel to the c axis. The positions of the iodine atoms are represented by the circles. The closest distance of approach between the two iodine atoms (its projection is indicated on the drawing by l) was calculated to be 3.99 Å. The next closest approach between two iodine atoms is along the c axis, and is equal to c_0 = 4.34 Å. Both of these values are reasonable and, in fact, are in excellent agreement with the distances found in the organic crystal iodoform. Hendricks[7] has calculated from I. Nitta's work on iodoform[8] that the closest approach of iodine atoms in adjacent molecules is 3.94 Å. and the next closest is 4.43 Å. Huggins and Noble[9] have found almost identical values from their study of iodoform. Thus the agreement is complete within the accuracy of the values of the parameters themselves, which in the case of each crystal is probably about ±0.1 Å.

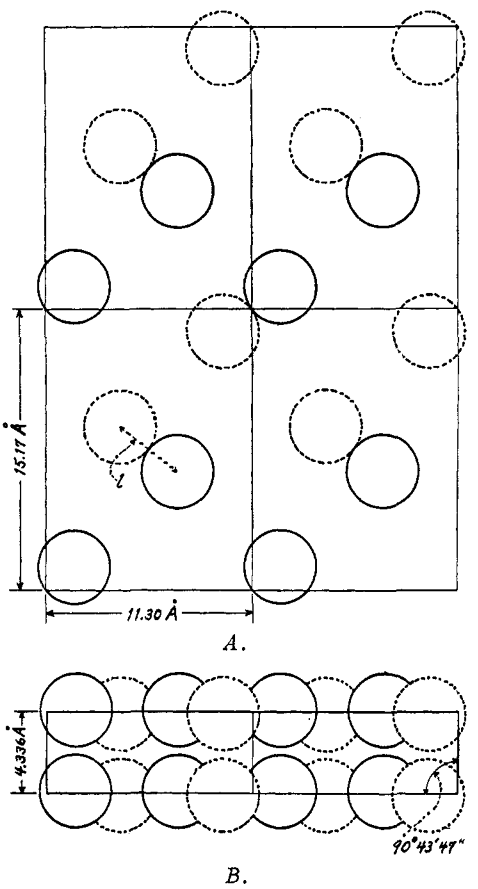


Fig. 2.—(*A*) Projection of four unit cells on (001) parallel to the c axis. The dotted circles represent iodine atoms at a distance of 0.087 Å. below the (001) plane, and the full circles iodine atoms at the same distance above (001). (*B*) Projection of two cells on (010).

From Fig. 2-A the two-fold screw axis and the glide plane perpendicular

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(7) Hendricks, *Chem. Reviews*, 436 (1930).

(8) Nitta, *Sci. Papers Inst. Phys.-Chem. Research* (Tokyo), **4**, 49 (1926).

(9) Huggins and Noble, *Am. Mineral.*, **16**, 519–25 (1931).

to it are evident. Also the pseudo-glide plane parallel to (100) is readily observed. The projection of the cell on (010) (Fig. 2-B) makes evident a pseudo-plane of symmetry parallel to (001). Thus the symmetry and pseudo-symmetry of the observed x-ray reflections are all accounted for by the resulting structure.

It is difficult to make any statement concerning the location of the remainder of the molecule in the cell. The diameter of the plane benzene ring exclusive of the hydrogen atoms is approximately 4.26 Å. Since the hydrogen atoms are believed to be in the plane of the ring of carbon atoms, the plane of the benzene ring cannot be parallel to the *c* axis. Further location of the remainder of the molecule is not profitable at this time.

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Summary

By the use of powder, Laue and oscillation photographs, the crystal structure of ortho-iodobenzoic acid has been investigated. It was found to have a 4-molecule cell with the following dimensions

$$a_0 = 11.30\ \text{Å.} \qquad b_0 = 15.17\ \text{Å.} \qquad c_0 = 4.336\ \text{Å.} \qquad \beta = 90^\circ\ 43'\ 47''$$

The corresponding axial ratios are $a:b:c = 0.7450:1:0.2863$ with $\beta = 90^\circ\ 43'47''$. The space group is C_{2h}^5. The iodine atoms are in the general positions with the following parameters: $x = 0.14$, $y = 0.08$ and $z = 0.02$. These lead to the closest distances of approach between iodine atoms of adjacent molecules of 3.99 Å. and 4.34 Å., values which are reasonable.

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