THE CRYSTAL STRUCTURE OF IODOFORM

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In this paper we wish to report the results of an x-ray investigation, made in 1926, of the crystal structure of iodoform. As our results are in complete accord with those obtained by Nitta,[1] whose work became known to us as ours was nearing completion, the presentation will be brief.

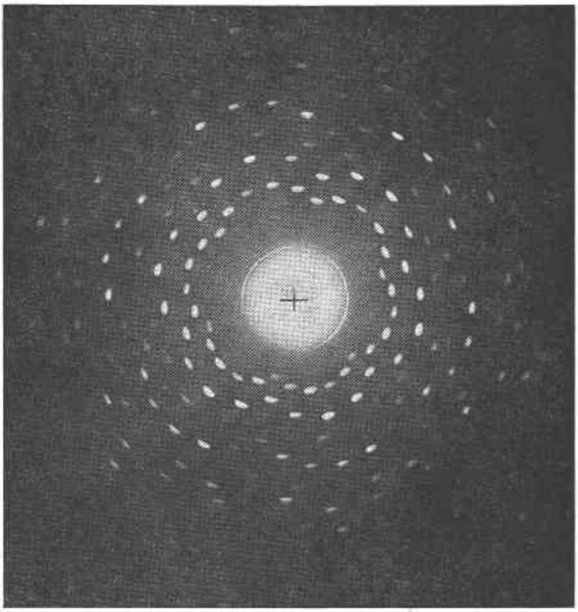

FIG. 1. Laue photograph taken with x-ray beam parallel to the c-axis.

Iodoform crystallizes in the hexagonal system.[2] The crystals used, obtained by recrystallization from acetone, showed faces of the forms $\{0001\}$ and $\{10\bar{1}1\}$. Laue photographs were obtained (1) with the x-ray beam (from a tungsten target) parallel to the c-axis (Fig. 1), and (2) with the beam making an angle of about 5° with that axis. Reflection spectra were obtained (3) from a (0001) face and (4) from a $(10\bar{1}1)$ face, a calcite spectrum being in each

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[1] Nitta, *Sci. Papers Inst. Phys. Chem. Res.* (Tokyo), **4**, 47, 1926.

[2] Groth, *Chemische Krystallographie*, **3**, 4.

case produced at the same time for comparison purposes. A reflection spectrum from (0001) was also obtained (5) without the calcite spectrum, an *a*-axis being in the axis of rotation (Fig. 2). For all of these spectra a molybdenum target *x*-ray tube was used and the crystal was oscillated at constant angular velocity through an angle of 20°.

The smallest unit cell (with either of the two possible orientations of the *a*-axes) which will permit the assignment of integral indices to all the reflections in the oscillating crystal photographs has the approximate dimensions $a_0 = 6.8$ Å and $c_0 = 7.5$ Å. Larger units would leave unexplained large classes of absences. The Laue data also lead to a unit cell of these dimensions. Smaller units would require for some of the reflections wave-lengths known to be absent from the incident *x*-ray beam. The comparison spectra with calcite gave $d_{0002} = 3.76_2$ Å and $d_{10\bar{1}1} = 4.64_5$ Å. From these can be calculated the values $a_0 = 6.81_8$ Å and $c_0 = 7.52_4$ Å, giving an axial ratio (c/a) of 1.10_4, in good agreement with the crystallographically

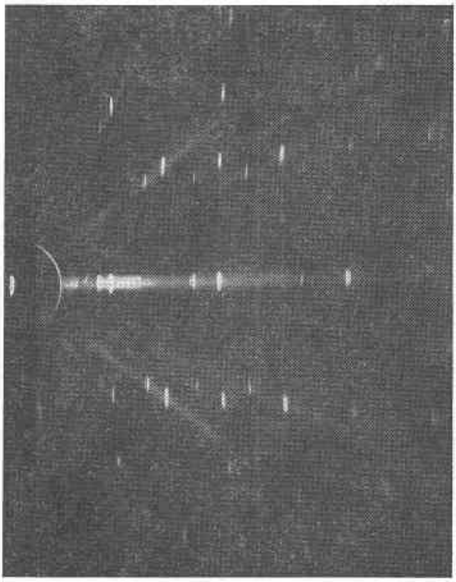

FIG. 2. Photograph obtained by oscillating a crystal about an *a*-axis. The lines in the principal spectrum are the (0002), (0004), (0006), and (0008) (Kβ only) reflections.

determined value,[3] of 1.1084. The density, calculated for two molecules per unit, is 4.29 g./cc. to be compared with the observed value[4] of 4.1 g./cc.

In view of the negligibly small reflecting power of carbon and hydrogen relative to that of iodine, one cannot be sure that the true unit of structure is not larger than this, but our data show that the arrangement of iodine atoms at least, can be described in terms of this size of unit. In our determination of the space group and of the parameters it has also been necessary to ignore the scattering produced by the lighter atoms.

The symmetry of the "symmetrical" Laue photograph (Fig. 1) is such as would only be produced by a structure isomorphous with one of the point groups $C_3^h(A_3 \cdot P)$, $C_6(A_6)$ or $C_6^h(A_6 \cdot P \cdot C)$. The basic lattice is the hexagonal, rather than the rhombohedral, since many reflections were observed for which $(2h+k+l)/3$ is not integral. Although the 2nd, 4th, 6th and 8th order reflections from (0001) were observed, with strong or medium intensities, no odd order reflections from this face were found. Other l odd reflections were present.

These observations eliminate[5] all arrangements of iodine atoms except one, which may be derived from either of the space groups C_6^6 or C_{6h}^2. The coordinates of the iodine atoms in this distribution are $xy0$; $y-x, \bar{x}, 0$; $\bar{y}, x-y, 0$; $\bar{x}\bar{y}\frac{1}{2}$; $x-y, x, \frac{1}{2}$; $y, y-x, \frac{1}{2}$.

Possible values of the parameters x and y were limited greatly by means of comparisons from the Laue photograph reproduced in Fig. 1, the procedure being similar to that outlined by Wyckoff.[6] All parameter values were considered which would make the distance of each iodine from the nearest trigonal axis between 1.8 and 2.1 Å. The comparisons listed in Table 1 eliminated all but three small regions, namely

(1) $x=.117-.135$; $y=.304-.338$
(2) $x=.298-.338$; $y=.185-.202$
(3) $x=.340-.365$; $y=.032-.058$

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[3] Pope, *J. Chem. Soc.*, **75,** 46, 1899.

[4] *Int. Crit. Tables,* **1,** 176.

[5] Wyckoff, Analytical Expression of the Results of the Theory of Space Groups, *Carnegie Inst. Publ.*, **318,** Washington, 1930; *Z. Krist.*, **63,** 507, 1926. Astbury and Yardley, *Phil. Trans. Roy. Soc.* (London), **A224,** 221, 1924. Mark, *Die Verwendung der Röntgenstrahlen in Chemie und Technik*, Barth (Leipzig), **1926,** pp. 392–393.

[6] Wyckoff, *The Structure of Crystals*. Chem. Cat. Co. (*New York,* **1924**) p. 217.

TABLE 1. USEFUL DATA FROM LAUE PHOTOGRAPH (1)

$\{hk\bar{i}l\}$	d_{hkl}	λ	Intensity
$23\bar{5}1$	1.33	.45	0.6
		.44	0.6
		.42	0.6
$32\bar{5}1$	1.33	.45	2.0
		.44	2.0
		.42	2.0
$41\bar{5}1$	1.27	.46	2.0
		.44	2.0
		.41	1.0
$14\bar{5}1$	1.27	.46	2.0
		.43	2.0
		.42	1.5
$25\bar{7}2$	.92	.48	.05
		.47	.05
		.44	.05
$16\bar{7}2$	.88	.43	.3
		.41	.2
		.40	.2
$61\bar{7}2$	.88	.43	.4
		.41	.4
		.40	.3
$62\bar{8}3$	.78	.45	.2
$34\bar{7}1$	.96	.27	0
		.26	0
$43\bar{7}1$	.96	.28	.15
		.26	.05

Comparisons from above:

$32\bar{5}1 > 23\bar{5}1$
$41\bar{5}1 > 23\bar{5}1$
$14\bar{5}1 > 23\bar{5}1$
$16\bar{7}2 > 25\bar{7}2$
$61\bar{7}2 > 25\bar{7}2$
$62\bar{8}3 > 25\bar{7}2$
$61\bar{7}2 > 16\bar{7}2$
$43\bar{7}1 > 34\bar{7}1$

At this point in the analysis we became aware of Nitta's work. He had determined the unit distances as $a_0 = 6.87$ Å and $c_0 = 7.61$ Å, had arrived at the same arrangement of iodine atoms and had calculated the parameter limits to be

$$x = .346 - .362;\ y = .038 - .056$$

with the most probable values as

$$x = .352;\ y = .047.$$

These parameter values are in good agreement with our set (3) above. On making calculations to ascertain whether or not any of his data are in disagreement with our parameter ranges (1) and (2) we found that this is true of his comparison $13\bar{4}1 > 31\bar{4}1$. The reflections from planes of these forms on our Laue photograph (1) are mixtures of first and second orders. Examination of photograph (2) however showed reflections from such planes having relative intensities agreeing with those obtained by Nitta (See Table 2).

TABLE 2. USEFUL DATA FROM LAUE PHOTOGRAPH (2)

$\{hk\bar{i}l\}$	d_{hkl}	λ	Intensity
$31\bar{4}1$	1.60	.46	1.0
		.43	1.0
$13\bar{4}1$	1.60	.41	3.0

Comparison from above: $13\bar{4}1 > 31\bar{4}1$

The distribution of iodine atoms arrived at is represented in Fig. 3. If it be assumed that the carbon and hydrogen atoms require

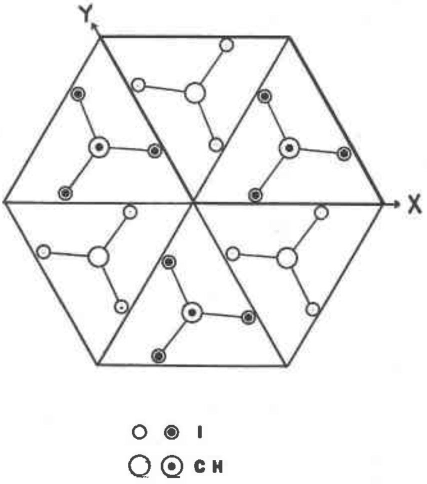

FIG. 3. A projection of a portion of the structure on a (0001) plane, showing the distribution of atomic centers and of C-I bonds.

neither a larger unit of structure nor a lower symmetry class than deduced from the experimental data and that the CHI_3 molecule maintains its identity in the crystal, it follows that the space group must be C_6^6 (rather than C_{6h}^2) and that the carbon and hydrogen atoms must be on three-fold symmetry axes. Of the two possible arrangements

$$\text{(a) } 0\,0\,u;\ 0, 0, \tfrac{1}{2}+u \qquad \text{(b) } \tfrac{1}{3}\,\tfrac{2}{3}\,u;\ \tfrac{2}{3}, \tfrac{1}{3}, \tfrac{1}{2}+u$$

the second, (b), is by far the more likely: the distance between iodine atoms in the same molecule is less than the distance between neighboring iodine atoms in different molecules and the molecules are in a "close-packed" array each roughly equidistant from 12 others rather than crowded together in parallel strings with each close to but two others and large distances between strings (an arrangement which should result in very ready cleavage parallel to the string axes). The parameter u_C is probably between .50 and .60, the latter being the value it would have if each carbon were at the center of a regular tetrahedron with iodines at three corners. This gives a C-I distance (from Nitta's "most probable" parameter values and our own unit distances) between 2.06 Å and 2.24 Å, agreeing well with the sum (2.12 Å) of half the I-I distance[7] (2.70 Å) in crystalline I_2 and half the C-C distance[8] (1.54 Å) in the diamond. The value of u_H is probably approximately $u_C+.15$, which would give a C-H distance of 1.1_3 Å, the value computed from band spectra assumed to be due to a CH molecule.[9] Each H is near the center of a group of 6 I atoms, three in the same molecule and three in adjacent molecules.

Each iodine center is 3.56 Å from the other two iodines in the same molecule and 4.39 Å from four, 4.38 Å from two, 4.46 Å from two, and 3.91 Å from two others in adjacent molecules. These last four distances are, as would be expected, not far from the distances between iodine atom centers in adjacent molecules in SnI_4[10] (4.21 Å), CdI_2[11] (4.21 Å), HgI_2[12] (4.10 Å) and I_2[7] (3.54 and 4.34 Å).

Lawrence Brockway and Linus Pauling of the California Institute of Technology have observed the scattering of Mo $K\alpha$ by a

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[7] Harris, Mack and Blake, *J. Am. Chem. Soc.*, **50,** 1583, 1928.

[8] W. H. Bragg and W. L. Bragg, *X-Rays and Crystal Structure,* G. Bell and Sons (London), p. 106.

[9] *Int. Crit. Tables,* **5,** 412.

[10] Dickinson, *J. Am. Chem. Soc.*, **45,** 958, 1923.

[11] Bozorth, *J. Am. Chem. Soc.*, **44,** 2232, 1922.

[12] Huggins and Magill, *J. Am. Chem. Soc.*, **49,** 2357, 1927.

saturated solution of iodoform in benzene. They obtained maxima, other than the benzene maxima, at 13° 13′ and 24° 15′ (total angles of diffraction), corresponding to a distance between iodine atoms in the molecule of 3.86 Å and 3.80 Å respectively, in each case ±0.2 Å, using Debye's formula for scattering by molecules.

The arrangement of carbons, of hydrogens, or of molecules considered as a whole is that of hexagonal close-packing, except for a contraction in the direction of the hexagonal axis from $c_0/a_0=1.63$ to $c_0/a_0=1.10$. Probably more significant however is the fact that the arrangement of iodine atoms is also approximately that of hexagonal close-packing. It would be exactly that if $x=.333$, $y=0$ and $c_0/a_0=1.633/\sqrt{3}=.943$.

SUMMARY

Using Laue and oscillating crystal x-ray photographs, the arrangement of iodine atoms in CHI_3 has been determined. The hexagonal unit cell has the dimensions $a_0=6.81_8$ Å, $c_0=7.52_4$ Å, and contains two molecules. The space group is C_6^6, the iodine atoms being in the positions

$$xy0;\quad y-x,\bar{x},0;\quad \bar{y},x-y,0;\bar{x}\bar{y}\tfrac{1}{2};\quad x-y,x,\tfrac{1}{2};\quad y,y-x,\tfrac{1}{2}$$

with $x=.346-.362$ and $y=.038-.056$. The carbon and hydrogen atoms are in all probability on three-fold symmetry axes, in positions

$$\tfrac{1}{3}\,\tfrac{2}{3}\,u;\ \tfrac{2}{3},\ \tfrac{1}{3},\ \tfrac{1}{2}+u$$

with u_C between .50 and .60 and with u_H approximately equal to $u_{C+}.15$.

The chief factors producing this type of structure seem to be the tendency of the large iodine atoms to form a close-packed assemblage and the tendency of the hydrogen ends of the molecules to be surrounded by iodine atoms.