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THE SPACE-GROUP AND MOLECULAR SYMMETRY OF β-BENZENE HEXABROMIDE AND HEXACHLORIDE

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Introduction

The small crystallographic symmetry of most organic compounds has limited the determination of their structures by crystal-structure researches. Yet many problems of structural organic chemistry can be so answered. We have determined the space-group and molecular symmetry of β-benzene hexabromide and hexachloride, and have obtained information of value in the interpretation of the geometrical isomerism of these compounds.

Both benzene hexabromide,[1] $C_6H_6Br_6$ and benzene hexachloride, $C_6H_6Cl_6$, crystallize in two modifications differing markedly in physical properties. The monoclinic forms, designated alpha, have been assigned the "*trans*" configuration.[2] The "*cis*" or beta modification of the hexabromide crystallizes in the cubic system, while the hexachloride has been reported to form[1] hexagonal crystals which are pseudocubic. Our investigation has been restricted to the beta forms.

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Preparation of Compounds

β-Benzene hexabromide was prepared by the method devised by Orndorff and Howells,[3] which consists of slow successive addition of small

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[1] Groth, "Chemische Krystallographie," Engelmann, Leipzig, **1910**, vol. **3**, pp. 603–606.

[2] Friedel, *Bull. soc. chim.*, [3] **5**, 130 (1891).

[3] Orndorff and Howells, *Am. Chem. J.*, **18**, 312 (1896).

amounts of bromine to a layer of benzene floating on a 1% solution of sodium hydroxide, the bromination being carried out near 0°. The alpha and beta forms, being insoluble in ethyl alcohol, were isolated from the lower bromination products by boiling with this solvent. The alpha form was removed by extraction with chloroform. The beta modification was purified by recrystallization from xylene. Small crystals 1 mm. thick showing the development {111} and {110} were obtained. The crystals melted sharply at 253°, and the yield was 0.1%.

β-Benzene hexachloride was prepared by the method described by Matthews.[4] It was separated from the alpha form by steam distillation, the alpha form being volatile. By recrystallization from xylene large crystals were obtained which melted sharply at 310°. Goniometric observations made on one of these crystals showed that it approximated very closely to a regular octahedron, the angle across any one of the edges being 70° 31′ (average).

The Crystal Structure of β-Benzene Hexabromide

The Unit of Structure.—Since bromine has an absorption edge at 0.918 Å., x-ray photographs made with MoK_α radiation were of very low intensity. Spectral photographs from (111) and (001) of β-benzene hexabromide did not give enough data for the determination of the size of the unit of structure. The powder photographic data, obtained by a prolonged exposure to MoK_α radiation, listed in Table I, require the edge of the unit cube to be 10.42 Å. Reflections from $(111)_n$ were absent in this photograph. The Laue data summarized in Table II further show that

Table I

Powder Photographic Data from β-Benzene Hexabromide (Cubic)

MoK_α radiation = 0.710 Å. Radius of Casette = 20.3 cm.

Plane	d/hkl	Intensity[a]	a_0 calcd. in Å.
221, 300	3.45	ms	10.35
320	2.89	ms	10.42
321	2.79	mw	10.44
330, 411	2.46	m	10.44
421	2.28	w	10.45
440	1.82	vvw	10.30
531	1.749	vvw	10.35
610	1.701	w	10.36
611, 532	1.672	vw	10.31
621, 443, 540	1.631	vvw	10.44
711, 551	1.46	vw-vvw	10.43
		Weighted mean a_0 =	10.42

[a] In the tables the following abbreviations are used: vs, very strong; s, strong; ms, medium strong; m, medium; mw, medium weak; w, weak; vw, very weak; vvw, very very weak.

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[4] Matthews, *J. Chem. Soc.*, **59**, 165 (1891).

TABLE II

LAUE PHOTOGRAPHIC DATA FROM β-BENZENE HEXABROMIDE (CUBIC)

X-ray beam 6° from normal to (100)

Plane	d/hkl Å.	Est. intensity	n Å.
304	2.089	1.0	0.35
105	2.049	0.0	.45
151	2.010	1.3	.43
441	1.819	0.15	.41
$30\bar{5}$	1.787	.0	.26
106	1.718	.20	.28
$2\bar{6}1$	1.631	.05	.45
710	1.477	.0	.41
$7\bar{3}1$	1.360	.8	.44
810	1.296	.05	.32
$7\bar{4}1$	1.286	.2	.42
182	1.249	.3	.40
$6\bar{6}1$	1.223	.8	.43
$8\bar{3}1$	1.211	.8	.35
109	1.154	.0	.44
910	1.154	.0	.25
920	1.133	.0	.48
$19\bar{2}$	1.126	.2	.28
$8\bar{5}1$	1.102	.1	.32
932	1.077	.05	.38
0.1.10	1.036	.0	.39
0.10.3	1.000	.0	.38
10.3.2	0.983	.2	.39
$3.\overline{11}.2$	.902	.2	.46
4.12.3	.804	.05	.24
11.5.5	.799	.1	.25
$0.2.\overline{13}$	.794	.15	.37
$13.\bar{2}.3$	.774	.05	.36
540[a]	1.632	.0	.47
450	1.632	.23	.39
560	1.337	.0	.32
650	1.337	.25	.41
760	1.131	.0	.39

[a] Data from a photograph made with x-ray beam 12° to normal to (100).

such a unit containing $4C_6H_6Br_6$ satisfactorily accounts for the observed reflections, since the values of n λ's calculated on the basis of this unit show the absence of wave lengths shorter than 0.24 Å., the minimum wave length present in the incident radiation. The density calculated on the basis of such a unit containing $4C_6H_6Br_6$ is 3.23, which is in good agreement with the value 3.197 determined by us by means of the suspension method of Retgers. A Coolidge tube with a tungsten anticathode operated at a peak voltage of 52 kv. was used throughout this investigation.

The Space Group.—The observation that a Laue photograph made with the x-ray beam normal to (100) did not show a four-fold axis of symmetry, but rather two planes of symmetry, requires the structure to be isomorphous with point groups T or T_h. Since reflections in the first order from planes with $h + k + l$ odd and $h + k$ odd were observed, the structure must be a simple cubic one derivable[5] from one of the following space groups: T^1, T^4, T_h^1, T_h^2, or T_h^6.

Reflection in the odd orders is required to be absent by the following space groups.

T^1, T_h^1—none
T^4—001 in odd orders
T_h^2—$hk0$ if $h + k$ is odd
T_h^6—$hk0$ if h is odd.

The observed reflections in the first order from (810), (0.2.13), (304), (106), (450) and (650) and the absence of reflection from (710), (105), (109), (910), (920), (0.3.10), (30$\bar{5}$), (0.1.10), (560), (540) and (760), although they were in position to reflect, indicate that T_h^6 is the space group from which the atomic arrangement can be derived. T_h^2 is definitely eliminated by the presence of reflections from (810), (304), (106), (650), and (0.2.13).

The Atomic Arrangement and the Symmetry of the Hexabromide Molecule

If one assumes the existence of molecules of $C_6H_6Br_6$ in the solid state, then the four molecules in the unit of structure must be crystallographically equivalent, their centers[6] being in the invariant positions 000, $\frac{1}{2}\frac{1}{2}0$, $0\frac{1}{2}\frac{1}{2}$, $\frac{1}{2}0\frac{1}{2}$. The symmetry of the molecule must be that of the point group C_{3i}, which has a three-fold axis and a center of symmetry (that is, a six-fold axis of the second sort). Since the space group T_h^6 can only give arrangements with four, eight, or twenty-four equivalent positions, the above symmetry requirements along with the assumption of the presence of molecules cannot be satisfied unless all the atoms of one kind are crystallographically equivalent, their positions being defined by the twenty-four equivalent positions of the space group.[7]

The distance of a particular atom of a molecule from a plane passing through the invariant position defining the molecular center and perpendicular to a microscopic axis of symmetry (referred to later as the plane of the molecule) is $(x + y + z)d_{100}$ (where x, y and z are the parameters defining the atomic positions). The significance of these observations will be discussed in a later section.

The Crystal Structure of β-Benzene Hexachloride

The investigation of this compound led to a result similar to that obtained in the case of β-benzene hexabromide. In this case, however, it

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[5] Wyckoff, "The Analytical Expression of the Theory of Space Groups," *Carnegie Inst. Publ.*, **318** (1922).

[6] Niggli, "Geometrische Kristallographie des Diskontinuums," Gebrüder Borntraeger, Leipzig, **1919**, p. 410.

[7] Arrangements involving six or more collinear atoms along the three-fold axis of one molecule are tacitly excluded as improbable.

was necessary to determine the crystallographic symmetry of the crystals, which had previously been reported to be hexagonal. The observation that two Laue photographs, one taken with the x-ray beam normal to (111) and the other with the x-ray beam normal to $(11\bar{1})$ of the *same* crystal, gave a three-fold axis of symmetry requires the crystal to be cubic. A Laue photograph made with the x-ray beam normal to (100) showed two planes of symmetry, this requiring the structure to be isomorphous with point groups T or T_h.

The size of the unit was determined from the spectral data listed in Table III and from the Laue data in Table IV, the analysis being similar to that

TABLE III

SPECTRAL DATA FROM β-BENZENE HEXACHLORIDE (CUBIC)

hkl	Line[a]	Order	Angle of reflection	*d/n* Å.	Intensity of reflection
111	β	n	3° 3.5′	5.930	m
	α	n	3° 26.5′	6.340	ms
	β	$4n$	12° 32′	5.816	w
	α_2	$4n$	14° 6.5′	5.816	m
	α_1	$4n$	14° 13′	5.800	w
	β	$5n$	15° 46′	5.810	w
	α_2	$5n$	17° 43.5′	5.815	ms
	α_1	$5n$	17° 48.5′	5.820	w
				Mean 5.815	

[a] In this table of spectral data, β indicates MoK_β, $\lambda = 0.6311$ Å.; α_1, MoK_{α_1}, $\lambda = 0.7078$; α_2, MoK_{α_2}, $\lambda = 0.7121$; α mean of α_4 and α_2, $\lambda = 0.710$.

TABLE IV

LAUE PHOTOGRAPHIC DATA FROM β-BENZENE HEXACHLORIDE (CUBIC)

X-ray beam 6° from normal to (111)

Plane	*d/hkl* Å.	Intensity	*n*λ Å.
043	2.014	0.1	0.46
034	2.014	.0	.40
$\bar{1}44$	1.754	2.0	.44
053	1.727	0.0	.34
$40\bar{5}$	1.573	.0	.30
$1\bar{3}\bar{6}$	1.486	.7	.36
$\bar{1}55$	1.410	.3	.30
371	1.311	.3	.38
$\bar{6}\bar{5}0$	1.289	2.5	.47
$\bar{6}05$	1.289	.0	.47
526	1.250	.2	.41
$41\bar{7}$	1.240	.8	.43
$56\bar{3}$	1.204	3.2	.48
075	1.172	.0	.30
$50\bar{7}$	1.172	.0	.25
$\bar{7}06$	1.092	.1	.38
$\bar{7}\bar{6}0$	1.092	.0	.37

TABLE IV (*Concluded*)

Plane	d/hkl Å.	Intensity	$n\lambda$ Å.
058	1.067	.0	.33
457	1.062	.2	.39
681	1.002	.4	.27
807	1.000	.0	.31
$93\bar{4}$	0.978	.15	.47
$76\bar{5}$	.960	.1	.33
1.10.5	.897	.05	.31
$\bar{9}07$	.884	.0	.41
$\bar{9}\bar{7}0$	.884	.0	.37
$86\bar{7}$	.825	.05	.28
$\bar{3}.13.8$	.685	.05	.41
$\overline{11}.4.11$	.605	.05	.29

given for β-benzene hexabromide. The edge, a_0, of the unit cube containing $4C_6H_6Cl_6$ is 10.07 Å. The density calculated on the basis of this unit is 1.88, in good agreement with the directly determined density[1] of 1.89. Reflection in the odd orders from the following planes (043), (650) and ($\bar{7}06$), and the absence of reflection from (053), ($40\bar{5}$), ($\bar{6}05$), (075), ($\bar{9}07$), ($\bar{9}\bar{7}0$), ($\bar{8}07$), ($50\bar{7}$), (034) and (058), even though they were in position to reflect in the first order, make it probable that the correct atomic arrangement is derivable from the space group T_h^6 (see preceding section).

Discussion of the Structures

In general, the required molecular symmetry (C_{3i}) of the (cubic) modifications of the hexahalides of benzene leads to a single geometrical configuration of the molecule, a representation of which is given in Fig. 1a. The surfaces of projection in this figure are two interpenetrating regular hexagonal prisms, having the common center O and coaxial along the c-axis. The a-axis of one of the hexagons is rotated through the angle θ from those of the other hexagon. The atomic positions are represented by two kinds of circles, all circles of one kind representing carbon atoms and those of the other kind bromine atoms. Since the hydrogen atoms need not necessarily conform to space symmetry, their positions are not designated; in general they would be placed upon a third regular hexagon in a similar position to the above two. The distance h of a particular kind of atom from the plane containing the a-axis and O, the center of symmetry of the molecule (the plane of the molecule) is $(x + y + z)d_{100}$, x, y and z being the parameters defining the atomic positions. This general configuration leaves three questions concerning distances unanswered; the length of the intercepts of the hexagons on the a-axis, and the values of h and of θ.

This general case can be simplified only on the basis of data not arising from the crystal structure investigation. Although such methods are often resorted to, their promiscuous use is doing much to lower the standards of such investigations. A possible simplification of the general case is given in Fig. 1b. In this case the two hexagonal prisms are brought into coincidence by making θ, 0°, and the a-axial intercepts equal.

The large black circles represent the atomic positions of the carbon atoms, the small black circles hydrogen atoms, and the large circles, bromine atoms. Such a configuration results in a "tetrahedral" carbon atom, gives reasonable atomic distances, and is not incompatible with the striking spectral data from (111).

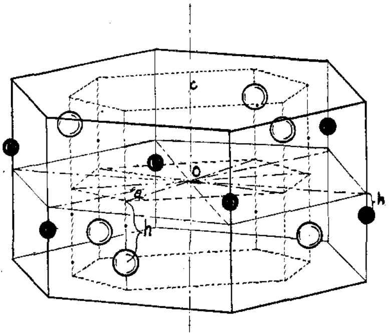

Fig. 1a.

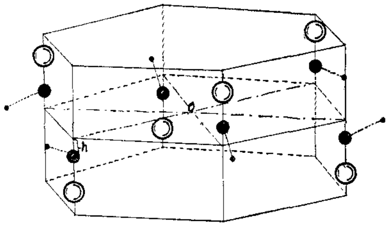

Fig. 1b.

Arrangement of the carbon atoms (large black dots) and halogen atoms (white circles) in molecule of $C_6H_6X_6$. The small black dots represent hydrogen atoms.

The unit of structure containing $4C_6H_6X_6$ is shown in Fig. 3. In this figure the large circles are to be replaced by Fig. 1a, the c-axis of the molecule being coincident with a microscopic axis of symmetry of the unit cell, while the center of symmetry, O, is placed at the center of a corresponding black circle. The microscopic axes of symmetry are represented by the light solid lines passing through the centers of the circles.

The structures previously assigned to the isomeric benzene hexachlorides by Friedel,[2] Figs. 2a and b, require all of the carbon atoms to be in one plane. In the case of the cubic form he stated that the higher crystallographic symmetry required the six chlorine atoms to be on the same side of the plane as shown in Fig. 2b. These conclusions were based upon two chemical methods often used in assigning spatial formulas, reactions and melting points. The relative amounts of the alpha (monoclinic) and beta (cubic) modifications of benzene hexachloride formed during prolonged chlorination of benzene were explained on the basis of the above formulas (Figs. 2a and b). While Friedel's mechanism of addition would not be acceptable now, his conclusions are still recognized. Orndorff and Howells,[3] for similar reasons, assigned identical structures to the benzene hexabromides. They used the additional criteria that the most symmetrical compound would have the least chemical reactivity (elimination of hydrogen bromide, etc.).

Our results as shown in Fig. 1a, do not eliminate the possibility of the carbon atoms, or even the halogen atoms, being co-planar. Such a specialization, however, would be a trivial case. A division of the halogen atoms so that four, five or six atoms would be on the same side of the "plane of the molecule" would not give the correct symmetry. The structures of Friedel are consequently considered incorrect.

We would like to point out that such methods of determining spatial configurations are artificial. A. Langseth[8] has recently considered the

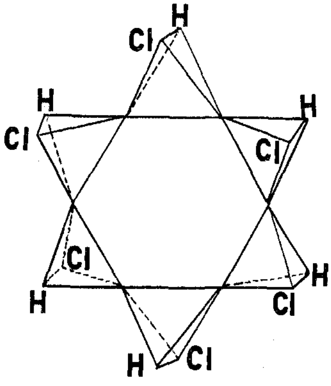

Fig. 2a.

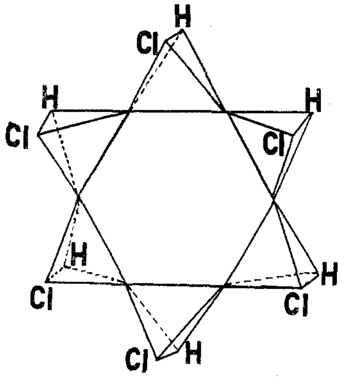

Fig. 2b.

correlation of physical properties and spatial isomerism. He concludes that regularity is observed in the case of the melting points only, *cis* modifications having in general the lower melting points. Our investigation corrects the discrepancy offered by the benzene hexahalides since we observe that *trans* (beta) modifications have the higher melting points. Such a classification depends upon the correctness of the previously assigned spatial formulas, and for this reason is of somewhat questionable nature. The arbitrary classification into *cis* and *trans* stereo-isomers would not be sufficient to identify all of the possible benzene hexachlorides (a third and fourth modification are known).[9]

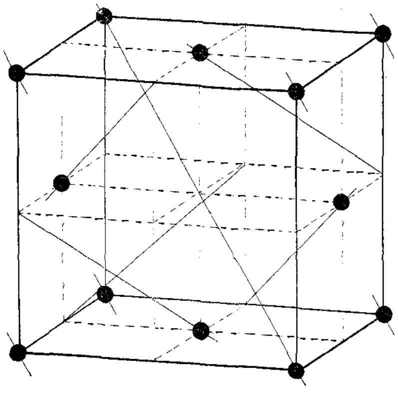

Fig. 3.—Replace circles by Fig. 2a.

Although use is often made of crystallographic symmetry consideration in assigning spatial formulas, such a method is open to serious questioning. Thus even though a molecular compound might be isomorphous with the cubic point group T, the symmetry of the molecule would not necessarily be greater than that of the triclinic point group C_1, which involves merely

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[8] Langseth, *Z. physik. Chem.*, **118,** 49 (1925).

[9] "International Critical Tables," McGraw-Hill Book Co., **1926,** Vol I.

the identical operation. A space determination by x-ray means, combined with the valid assumption of the presence of molecules in the crystals of organic substances will allow the investigator to determine the minimum symmetry of such molecules. A complete determination in the case of organic compounds is a very difficult task, restricted at present to those compounds of high symmetry and simple molecular formulas.

It is of interest to note that Mohr's[10] theory of "Strainless Rings" as applied to cyclohexane and its derivatives is not compatible with our conclusions, in so far as the solid state is concerned. His three-dimensional formulas, which seem to give a satisfactory explanation for the isomerism of decahydronaphthalene, have a center of symmetry in one case, but not a plane of symmetry. Four carbon atoms of a particular cyclohexane ring are co-planar, the 1,4 carbon atoms being equidistantly placed above and below this plane. Such a representation would not be tenable on the basis of our conclusions. A promiscuous interconversion of molecular configurations between two such widely separated forms as represented by Fig. 1a and as required by Mohr's theory, would probably not be possible. Since Mohr's arguments are based on cyclohexane it would be of value to point out that this compound is also cubic within a narrow temperature range, and for that reason is suceptible to investigation (a low temperature is required). This compound is being studied at the present time.

Conclusion

Crystals of the cubic modification of benzene hexabromide and -chloride have been investigated by means of Laue, powder and spectral x-ray photographs. The edges of the unit cubes containing $4C_6H_6X_6$ are 10.42 Å. and 10.07 Å., respectively. The atomic arrangement has the space-group symmetry T_h^6. The symmetry of the molecule is that of the point group C_{3i}, which requires a three-fold axis and a center of symmetry.

The conclusions concerning the molecular symmetry of these compounds necessitate a revision of the ideas relating to their geometrical isomerism.

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[10] Mohr, *J. prakt. Chem.*, **98**, 315 (1918). Sachse, *Ber.*, **23**, 1363 (1890); *Ann. Repts. Chem. Soc.*, **20**, 103 (1923); **21**, 92 (1924).