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## The Crystal Structure of *p*-Dichlorobenzene

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The structure of *p*-dichlorobenzene has been determined by means of two electron-density projections. It is found that this compound is isostructural with *p*-dibromobenzene whose structure was previously determined by the authors. All the atoms of each molecule are in the same plane, the benzene ring is a plane regular hexagon of 1.40 Å side, and the chlorine atoms are on the hexagon diagonal.

### 1. Introduction

In previous researches (Bezzi & Croatto, 1942; Croatto & Bezzi, 1949b) we have determined the crystal structure of *p*-dibromobenzene, using X-ray methods with Fourier-Bragg analysis. In the present work we have obtained the structure of *p*-dichlorobenzene. This concludes a program of researches directed not only to establishing the crystalline structure of such substances, but also to throwing light on some controversial problems in isomorphism.

On the one hand Bruni & Gorni (1899, 1900 *a b*), in well known classical researches, consider *p*-dichlorobenzene and *p*-dibromobenzene as typical isomorphous substances, from consideration of their analogous formulae and the close similarity of their crystal constants; on the other hand Hendricks (1933) believed that he had shown that these two substances differed markedly in their crystalline structures. The X-ray work of Hendricks on these substances was carried out by the method of 'trial and error'.

It is worth noting that Hendricks was able to determine only the parameters of the halogens with certainty, and found that they were practically the same for the two substances. In this halogen lattice there are two positions which can be occupied by the benzene ring. Hendricks believed that the benzene rings did not occupy the same positions in both substances, but that one position was occupied in *p*-dichlorobenzene and the other in *p*-dibromobenzene.

It must be observed that Hendricks's choice be-

tween these two positions was made on the basis of X-ray data only in the case of *p*-dichlorobenzene. The choice between the two possible positions for the benzene ring in *p*-dibromobenzene was made on the basis of the optical properties of the crystals.

It seems opportune to take up this study of the above substances again, by means of development in Fourier series.

### 2. Determination of the structure of *p*-dichlorobenzene

The X-ray work on *p*-dichlorobenzene has been carried out with crystals sealed in small tubes of Lindemann glass, to avoid evaporation. We have taken rotation and Weissenberg photographs with rotation about the *b* and *c* axes.

The space group is  $C_{2h}^5-P2_1/a$ ; the unit cell contains two molecules of  $C_6H_4Cl_2$ , and has the following dimensions:

$$a = 14.80, \quad b = 3.99, \quad c = 5.78 \text{ \AA}, \quad \beta = 113^\circ,$$

in good agreement with the previous data of Hendricks.

The four points in general positions of the space group  $C_{2h}^5-P2_1/a$  have the co-ordinates:

$$\begin{aligned} x, y, z; & \quad \frac{1}{2}+x, \frac{1}{2}-y, z; \\ \bar{x}, \bar{y}, \bar{z}; & \quad \frac{1}{2}-x, \frac{1}{2}+y, z. \end{aligned}$$

The reflexions on the Weissenberg photographs were identified by the method of the reciprocal lattice and

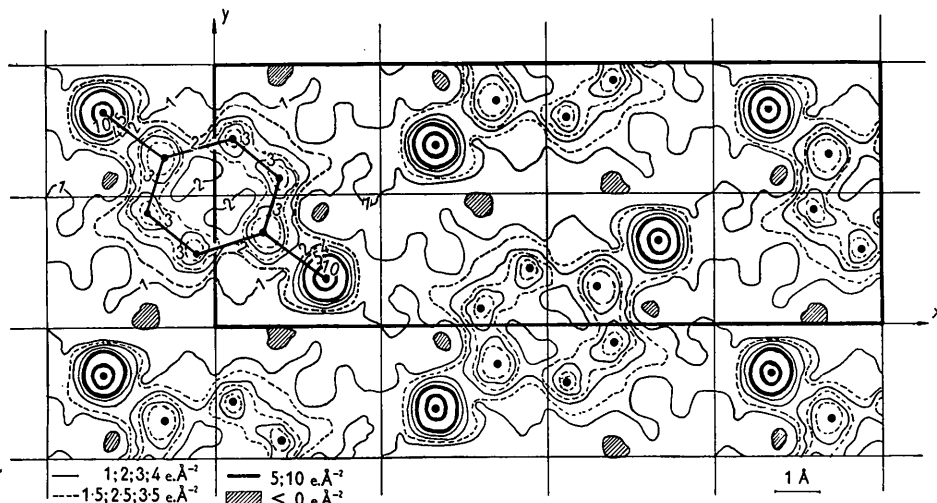


Fig. 1. Electron-density projection on absolute scale on the (001) plane calculated with the temperature factor with  $B = 4 \times 10^{-16} \text{cm}^2$ . The schematic projection of a molecule is also represented.  $\bullet$ : peak of the function.



Fig. 2. Electron-density projection on absolute scale on the (010) plane calculated with the temperature factor with  $B = 4 \times 10^{-16} \text{cm}^2$ . The schematic projection of a molecule is also represented.  $\bullet$ : peak of the function.

Table 1. Atomic parameters of the *p*-dichlorobenzene and the *p*-dibromobenzene structures

Atom	<i>p</i> -Dichlorobenzene; parameters deduced from the projections			<i>p</i> -Dibromobenzene; parameters by Bezzi & Croatto		
	<i>x</i>	<i>y</i>	<i>z</i>	<i>x</i>	<i>y</i>	<i>z</i>
Halogen	0.162	0.180	0.977	0.169	0.170	0.976
C <sub>1</sub>	0.072	0.345	0.979	0.074	0.355	0.992
C <sub>2</sub>	0.095	0.570	0.145	0.097	0.571	0.197
C <sub>3</sub>	0.030	0.711	0.203	0.021	0.716	0.203

the graphical method. Their intensities were measured photometrically.

The Fourier-Patterson projections calculated from these data have allowed the determination, to a first approximation, of the parameters of the chlorine atoms, as follows:

$$x = 0.168, y = 0.179, z = 0.960.$$

The details of this first part of the work have been published in two notes by our collaborators (Bua, 1951; Bua & Scatturin, 1951). In these notes it has

also been possible to decide which of the two possible positions is occupied by the benzene ring. This position is the same as that which we have previously found for *p*-dibromobenzene.

To a first approximation, the maxima arising from carbon atoms in the Fourier-Patterson projections are in agreement with the projection of the benzene ring disposed between the halogens exactly as we have already found for *p*-dibromobenzene. This fact has allowed us to calculate the signs of the structure factors using for chlorine the parameters determined

from the Fourier-Patterson projections, and assuming for the carbon atoms the co-ordinates which we have found for *p*-dibromobenzene.

It has not been possible to proceed in this case as we have done for *p*-dibromobenzene, i.e. to determine the signs of the structure factors from the co-ordinates of the halogen, because the atomic number of chlorine is not sufficiently greater than that of carbon to be sure that the sign of the structure factor always coincides with the sign of  $F_{Cl}$ .

The electron-density projections on the 001 and 010 planes calculated on this way have permitted an approximate determination of the structure.

The definitive electron-density projections have then been calculated after correcting the  $F$  values with thermal factors and transferring them suitably to the absolute scale, as we have already shown (Croatto & Bezzi, 1949a).

The atomic parameters, obtained by graphical interpolation from the electron-density projections of Figs. 1 and 2, are given in Table 1.

The calculated structure factors for the reflexions

$hk0$  and  $h0l$  are given in Tables 2 and 3 along with the observed  $|F|$ 's which have been adjusted so that

$$\sum |F|_c = \sum |F|_o.$$

The values for the expression

$$\sum (|F|_o - |F|_c) \div \sum |F|_o$$

are respectively 0.23 and 0.20.

In Table 1 are given, for purposes of comparison, the atomic parameters of *p*-dibromobenzene previously determined by us. As may be seen, for these two substances the values of the corresponding parameters are very similar and the differences are attributable to the different sizes of the two halogens. To the same fact may be attributed the small difference between the two elementary cells, from which it must be concluded that *p*-dichloro- and *p*-dibromobenzene have identical structures, contrary to the statement of Hendricks, and that the assumption of Bruni & Gorni, that these two substances can be considered as typical examples of isomorphous substances, is correct.

Table 2. *Observed and calculated values of the structure factors*

$hk0$	$ F _o$	$F_c$	$hk0$	$ F _o$	$F_c$	$hk0$	$ F _o$	$F_c$
020	40.8	-39.9	510	20.8	+20.2	950	18.0	-20.1
040	16.0	- 8.8	520	29.3	+30.7	10,0,0	16.9	-21.7
060	22.1	+24.3	530	12.6	-12.7	10,1,0	32.3	+31.5
110	25.0	-18.6	540	20.7	-29.8	10,2,0	14.6	+19.2
120	38.5	-33.2	600	23.9	+27.4	10,3,0	11.7	- 8.4
130	11.1	- 8.0	610	9.4	+10.1	10,4,0	9.7	+ 3.3
140	18.5	+24.2	620	29.3	-29.3	11,1,0	9.6	- 1.6
160	10.9	-13.3	630	8.7	- 9.3	11,2,0	14.1	+16.8
200	10.8	+15.0	660	17.0	+23.3	11,3,0	10.1	- 6.8
210	37.7	-43.9	710	23.4	+19.4	11,4,0	15.4	-23.8
220	8.1	+ 2.8	720	22.1	-17.3	11,5,0	7.4	+ 6.3
230	14.9	+12.6	730	22.7	-24.2	12,0,0	31.8	+31.7
250	19.8	+23.3	740	25.2	+30.2	12,1,0	17.6	+16.4
310	26.0	-25.0	800	21.5	-16.7	12,2,0	14.3	-15.1
330	39.8	+43.6	810	20.8	-24.8	12,3,0	9.6	- 2.0
340	11.9	- 4.2	820	15.9	+ 8.4	13,2,0	22.1	-17.8
350	18.4	-28.7	830	9.5	- 0.3	13,4,0	10.5	+15.6
400	24.6	-35.0	850	9.5	+13.2	14,0,0	14.6	- 4.3
410	34.4	+37.6	910	21.4	-15.5	14,1,0	19.0	-22.9
420	9.2	+ 5.5	920	16.3	-10.1	15,3,0	11.8	+23.5
430	14.4	- 7.9	930	20.9	+25.4	16,0,0	21.2	-25.2
440	14.5	+ 7.8	940	11.6	+15.3	16,1,0	10.4	+11.7

Table 3. *Observed and calculated values of the structure factors*

$h0l$	$ F _o$	$F_c$	$h0l$	$ F _o$	$F_c$	$h0l$	$ F _o$	$F_c$
001	50.6	+87.2	402	30.4	-36.5	80 $\bar{3}$	33.6	-30.8
002	28.3	+36.4	40 $\bar{2}$	15.0	-12.6	80 $\bar{4}$	25.1	-26.5
003	24.3	+25.3	40 $\bar{3}$	17.7	-10.6	10,0,0	19.6	-21.7
200	12.5	+15.0	600	27.8	+27.4	10,0,1	25.6	-27.6
201	21.7	-13.5	601	21.8	+21.2	10,0,2	25.8	-26.5
20 $\bar{1}$	16.7	+ 7.4	60 $\bar{1}$	32.2	+34.6	10,0,3	18.7	-16.9
202	24.1	-15.4	602	21.5	+23.6	12,0,0	36.9	+31.7
20 $\bar{2}$	28.9	-21.7	60 $\bar{2}$	29.7	+29.6	12,0,1	20.4	+23.2
20 $\bar{3}$	32.9	-29.3	60 $\bar{3}$	25.4	+24.9	12,0, $\bar{1}$	40.0	+42.8
20 $\bar{4}$	20.3	-26.1	800	25.0	-16.7	12,0, $\bar{2}$	34.0	+42.3
400	28.6	-35.0	801	14.2	-11.1	12,0, $\bar{3}$	27.9	+32.0
401	41.4	-45.3	80 $\bar{1}$	29.7	-21.5	14,0,0	17.0	- 4.3
40 $\bar{1}$	16.2	-14.7	80 $\bar{2}$	36.7	-28.9	16,0,0	24.6	-25.2

The spatial structure is represented in Fig. 3.

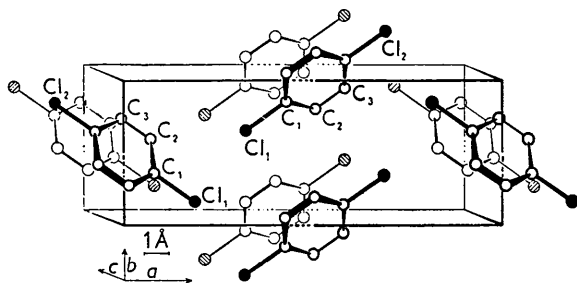


Fig. 3. Perspective representation of the structure of *p*-dichlorobenzene.

### 3. Shape and position of the molecules of *p*-dichlorobenzene, and interatomic distances

At this point we have the opportunity to decide whether the atomic parameters given in Table 1 are in agreement with the hypothesis that the molecules of *p*-dichlorobenzene have hexagonal, regular and plane benzene rings, with the chlorine atoms aligned on a diagonal, and of finding out the extent and nature of possible deviations from this ideal model. It also seems opportune to determine the distances between the various atoms of one molecule, and of different molecules, in order to compare them with the values deduced from our structure of *p*-dibromobenzene.

By the usual methods of analytical geometry we have determined the acute angles which the mean plane of the molecule makes with the three planes 100, 010 and 001, and the orthogonal co-ordinates ( $\xi$ ,  $\eta$ ,  $\zeta$ ) expressed in Ångström units for all the atoms, as shown in Table 4.

We have chosen the new system of axes ( $\xi$ ,  $\eta$ ,  $\zeta$ ), putting the origin at the point of intersection of the crystallographic axis  $b$  with the mean plane of the

Table 4. Coordinates of the eight atoms of the molecule of the *p*-dichlorobenzene referred to the axes  $\xi$ ,  $\eta$ ,  $\zeta$  (Values in Ångström units)

Atom	$\xi$	$\eta$	$\zeta$
Cl <sub>1</sub>	3.053	-0.215	-0.034
Cl <sub>2</sub>	-3.048	0.208	0.029
C <sub>1</sub>	1.413	-0.163	-0.010
C <sub>2</sub>	0.749	1.134	0.077
C <sub>3</sub>	-0.565	1.313	-0.063
C <sub>4</sub>	-1.408	0.156	0.006
C <sub>5</sub>	-0.744	-1.141	-0.081
C <sub>6</sub>	0.571	-1.320	0.059

molecule ( $\pi$ ), taking as the  $\xi$  axis the line of intersection of the plane  $\pi$  with the crystallographic plane ( $a$   $b$ ), and placing the  $\eta$  axis on the plane  $\pi$ , and the  $\zeta$  axis perpendicular to this plane.

The intercepts which the  $\pi$  plane makes on the  $x$ ,  $y$ ,  $z$  axes are respectively as follows:

$$A = +4.36 \text{ \AA}, \quad B = +2.89 \text{ \AA} \text{ (calc. } = \frac{1}{2}b = +2.89 \text{ \AA)}, \\ C = -1.42 \text{ \AA},$$

and the acute dihedral angles between the plane  $\pi$  and the three crystallographic planes are as follows:

$$\widehat{\pi(001)} = 31^\circ 52', \quad \widehat{\pi(010)} = 63^\circ 56', \quad \widehat{\pi(100)} = 86^\circ 20'.$$

The values  $\zeta$  in Table 4 all prove to differ from zero only by hundredths of an Ångström unit so that one may conclude that the coplanarity of all atoms of the molecule is established.

The projection of the molecule on the  $\pi$  plane is shown in Fig. 4, in which are also indicated the positions which the carbon atoms should occupy if they are at the vertices of a regular hexagon of side 1.40 Å.

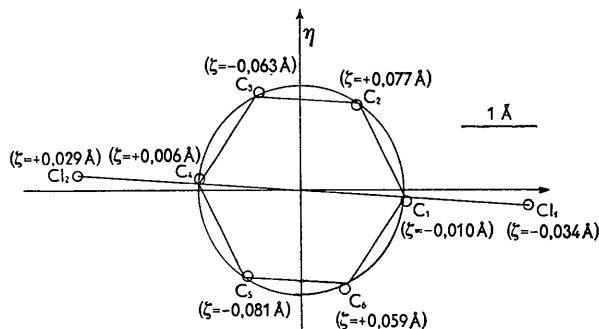


Fig. 4. On the figure are drawn the projections (O) of the atoms of a  $C_6H_4Cl_2$  molecule on its mid plane and a regular hexagon among the chlorine atoms.

In Table 5 the single interatomic distances determined experimentally are given.

Table 5. Interatomic distances

<i>p</i> -Dichlorobenzene	
Cl-Cl of different molecules	3.85 Å
Cl-Cl of one molecule	6.12 Å
Cl-C <sub>1</sub> of one molecule	1.64 Å
Average distance between neighbouring C atoms	1.40 Å
<i>p</i> -Dibromobenzene	
Br-Br of different molecules	3.76 Å
Br-Br of one molecule	6.50 Å
Br-C <sub>1</sub> of one molecule	1.85 Å

It can be seen that the Cl-Cl distance in one molecule is in perfect agreement with the value of 6.10 Å reported by Schoppe (1936) for work in the gas phase. The value of 1.40 Å found for the C-C distance is also the normal one.

This is the case for the molecule whose centre falls on the origin of the 010 projection. For the molecule whose centre falls on the origin of the 100 projection the three acute angles are the same as for the other, noting that the three intercepts are:

$$A = +7.41 \text{ \AA} \text{ (calc. } = \frac{1}{2}a = 7.40 \text{ \AA)}, \\ B = -4.91 \text{ \AA}, \quad C = -2.41 \text{ \AA}.$$

It is to be observed that the data of Hendricks are substantially confirmed in so far as concerns the coordinates of the halogens and the pair of halogens between which are the benzene rings. There is, however, disagreement in the orientation and shape of the benzene rings, which, according to Hendricks, should be hexagonal strongly deformed rings, almost parallel to the 001 plane.

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## An Orthogonal Unit Vector Triplet Associated with a General Lattice\*

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It is shown that there exists an orthogonal unit vector system  $\mathbf{E}$  and a symmetric matrix  $\gamma$  (together with its inverse  $\gamma^*$ ) such that the four expressions

$$\mathbf{a} = \gamma\mathbf{E}; \quad \mathbf{E} = \gamma\mathbf{a}^*; \quad \mathbf{a}^* = \gamma^*\mathbf{E}; \quad \mathbf{E} = \gamma^*\mathbf{a}$$

give the transformations between the systems  $\mathbf{a}$ ,  $\mathbf{a}^*$  and  $\mathbf{E}$ . The  $\gamma$ -matrices are then defined by the matrix equations  $\gamma^2 = \mathbf{g}$  and  $\gamma^{*2} = \mathbf{g}^*$ . The solutions are given explicitly for all two-dimensional nets and for all symmetrical three-dimensional lattices. Methods are suggested for the numerical calculation for the triclinic lattice. Uses for the  $\mathbf{E}$ -systems in crystal calculations are also discussed.

This paper is concerned with normal orthogonal vector triplet systems  $\mathbf{E}_i$  which are unique among the infinitely many possible normal orthogonal systems  $\mathbf{e}_i$  in the sense that the linear transformation which expresses the triplet  $\mathbf{E}_i$  in terms of  $\mathbf{a}_i$  is the same as that which expresses the  $\mathbf{a}_i^*$  in terms of the  $\mathbf{E}_i$ .

Although little application has as yet been made of these systems, their theoretical interest seems to merit a presentation of their properties.

### Properties of the $\mathbf{E}$ -systems

For the axial system  $\mathbf{a}_i$ , represented in matrix notation by the symbol  $\mathbf{a}$ , the metric tensor has a matrix representation  $\mathbf{g}$  with components

$$g_{ij} = (\mathbf{a}_i\mathbf{a}_j) \quad (1a)$$

while the determinant of the matrix  $\mathbf{g}$  has the value  $g$ . Similarly the reciprocal system  $\mathbf{a}_i^*$  is represented by the matrix symbol  $\mathbf{a}^*$  and has for reciprocal metric

tensor the matrix  $\mathbf{g}^*$  with components

$$g_{ij}^* = (\mathbf{a}_i^*\mathbf{a}_j^*), \quad (1b)$$

with determinant  $g^*$ . The matrix  $\mathbf{g}^*$  is thus the inverse of  $\mathbf{g}$ , i.e.

$$\mathbf{g}\mathbf{g}^* = \mathbf{1} \quad (2a)$$

and

$$g g^* = 1. \quad (2b)$$

It is well known (cf. Ewald, 1923, note 1) that

$$\mathbf{a} = \mathbf{g}\mathbf{a}^* \quad (3a)$$

and also that

$$\mathbf{a}^* = \mathbf{g}^*\mathbf{a}. \quad (3b)$$

We now define a vector system  $\mathbf{E}$  (without further specification of its properties), and a matrix  $\gamma$  with components  $\gamma_{ij}$  such that

$$\mathbf{a} = \gamma\mathbf{E} \quad (4a)$$

and

$$\mathbf{E} = \gamma\mathbf{a}^*. \quad (4b)$$

If  $\gamma^*$  is the inverse matrix to  $\gamma$  we have

$$\mathbf{a}^* = \gamma^*\mathbf{E} \quad (5a)$$

and

$$\mathbf{E} = \gamma^*\mathbf{a}. \quad (5b)$$

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