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Structure of the Monoclinic Form of *p*-Dichlorobenzene at Low Temperature

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The structure of the monoclinic form of *p*-dichlorobenzene has been determined at low temperature. Within the limits of experimental error it has been found that the benzene ring is a plane regular hexagon with side 1·39 Å. An anisotropic thermal vibration is found for the atoms Cl and C_1.

Introduction

The standard error of an atomic coordinate in structural analysis is not only a function of the reliability index, but also diminishes with the increase of the curvature of the electron density at peak centers (Cruickshank, 1949). It is evident that, in order to reduce the standard error in the final coordinates, the temperature at which diffracted intensities are collected should be lowered. This has been experimentally demonstrated by Burbank (1953) and later by Hirschfeld & Schmidt (1956). Using the advantages of low-temperature structural analysis, we have reexamined the monoclinic modification of the *p*-dichlorobenzene already described by Croatto, Bezzi & Bua (1952), in order to carry out the refinement to the limits of possibility.

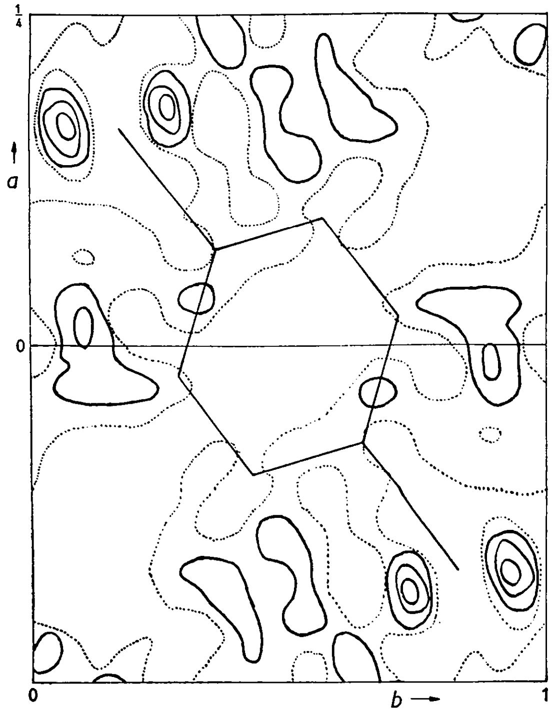

Fig. 1. (F_o-F_c) projection on (001) showing the anisotropic vibration of the Cl atom. Contours are drawn at intervals of 0·2 e.Å^{-2}, starting with 0·2 e.Å^{-2} (dotted lines).

During the course of refinement a note by Housty & Clastre (1957) appeared, regarding the structure of the triclinic form of *p*-dichlorobenzene existing at 30·8 °C. The authors, in agreement with Croatto, Bezzi & Bua (1952) find that the molecule is not planar, and has angles of 4° between bonds C–C and the mean plane of the molecule and that various bonds C–C of the benzene ring have appreciably unequal lengths.

Experimental and crystal data

The *p*-dichlorobenzene crystals were obtained from the melt in Lindemann glass. The experimental data were collected at a temperature of −140 °C. using the technique described by Post, Schwartz & Fankuchen (1951).

The crystal belongs to the space group C_{2h}^5–$P2_1/a$ with two molecules in the unit cell and has the following lattice constants:

at $t°$ = −140 °C.	at $t°$ = +20 °C.
a = 14·63±0·06 Å	a = 14·80±0·06 Å
b = 5·66±0·03 Å	b = 5·78±0·03 Å
c = 3·89±0·02 Å	c = 3·99±0·02 Å
β = 111° 45′±20′	β = 113° 0′±20′

The $h0l$ and $hk0$ intensities have been collected in the precession camera with radiation Mo $K\alpha$ and in the Weissenberg camera with Cu $K\alpha$ radiation. The intensities were integrated in a photometer and corrected by the usual Lorentz and polarization factors. The F_o have been put on an absolute scale using the structure factors calculated by Croatto, Bezzi & Bua (1952). The coordinates derived from the first maps of electron density gave a reliability index 0·19 for the projection on (001) and 0·18 for the projection on (010). For the calculation of F_c, atomic scattering factors given by McWeeny (1951) were used.

Refinement of projection on (001)

The refinement of this projection has been carried out by successive Fourier difference syntheses. In the first three stages corrections were introduced in the coordinates of the carbon atoms. With these adjustments R was reduced to 0·15. From Fig. 1 it can be seen that there was evidence of an anisotropic thermal vibration of the Cl atom with maximum vibration in a direction nearly parallel to the y axis of the cell. Therefore an experimental atomic scattering factor was calculated on the basis of the formula derived by Helmholtz (1936).

$$f_t = f_0 \exp\left\{-\left[(A+B\cos^2\varphi)\frac{\sin^2\theta}{\lambda^2}\right]\right\}$$

in which f_t is the experimental atomic scattering factor and f_0 is the scattering factor of a stationary atom, A and B are constants for reflecting planes parallel and perpendicular to the direction of maximum vibration respectively, and φ is the angle between the direction of maximum vibration and the reciprocal-lattice vector. Values of the constants A and B were found by calculation of the one-dimensional Fourier transform of the electron density in the directions of minimum and maximum vibration respectively. Recalculation of structure factors on this basis reduced R to 0·12. For the C atom bonded directly to Cl, the difference synthesis can be interpreted by assuming the existence of maximum vibration parallel to that of the Cl atoms. The introduction of an experimental atomic scattering factor did not give appreciable improvement of the reliability index. A fourth difference synthesis contained maxima which have been interpreted as positions of the two hydrogen atoms, and the introduction of the contribution of hydrogen atoms and some adjustments of the carbon atoms reduced R to the final value of 0·09.

Refinement of projection on (010)

From the coordinates calculated from the first electron-density map the signs of four F's (out of 62) were changed. With these sign changes and the use of the calculated value for the very strong 001 reflection, for which it was impossible to deduce the experimental value, a new Fourier synthesis was calculated and this gave new coordinates with which R fell to 0·14. This synthesis in spite of the low temperature factor did not resolve the carbon atoms C_1 and C_2. Therefore it was decided to calculate further difference syntheses,

Table 1. *Final atomic coordinates*

Atom	x/a	y/b	z/c
Cl_1	0·167	0·172	0·973
C_1	0·074	0·357	0·991
C_2	0·098	0·559	0·187
C_3	0·023	0·712	0·191
H_2	0·155	0·594	0·346
H_3	0·034	0·843	0·337

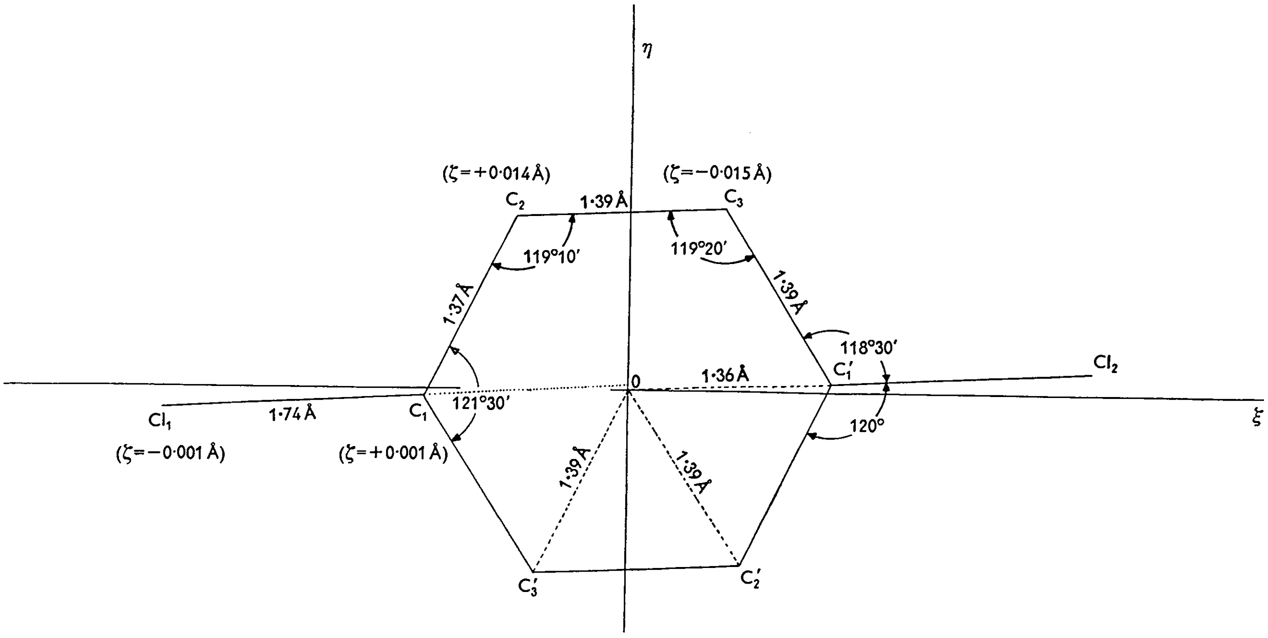

Fig. 2. Projection of the p-dichlorobenzene molecule on its mean plane. Bond lengths, angles and distances ζ from this plane are also drawn.

Table 2. *Observed and calculated structure factors for* p-*dichlorobenzene*

h k l	F_o	F_c
2 0 0	8,8	+ 9,4
4 0 0	25,0	-27,5
6 0 0	28,9	+30,1
8 0 0	20,4	-21,1
10 0 0	8,9	- 8,1
12 0 0	32,8	+33,0
14 0 0	13,4	-13,7
16 0 0	15,5	-14,9
1 1 0	13,4	-15,1
2 1 0	41,6	+41,0
3 1 0	19,0	-21,2
4 1 0	33,1	-33,3
5 1 0	23,9	+22,7
6 1 0	1,9	- 1,5
7 1 0	17,6	+15,3
8 1 0	15,9	+17,6
9 1 0	18,0	-17,3
10 1 0	34,3	-32,8
11 1 0	-	+ 0,1
12 1 0	9,7	- 9,3
13 1 0	2,8	+ 3,1
14 1 0	11,3	+12,6
15 1 0	9,2	-7, 6
16 1 0	13,5	-15,1
0 2 0	25,9	-29,1
1 2 0	34,2	+34,3
2 2 0	-	+ 2,1
3 2 0	-	-
4 2 0	2,8	- 2,9
5 2 0	32,0	-28,1
6 2 0	28,7	-26,6
7 2 0	22,9	+23,1
8 2 0	9,5	+ 8,4
9 2 0	4,0	+ 5,1
10 2 0	11,1	+10,8
11 2 0	10,4	- 8,8
12 2 0	10,9	-11,9
13 2 0	24,6	+23,5
1 3 0	5,5	- 6,9
2 3 0	4,2	- 6,1
3 3 0	38,1	+38,3
4 3 0	5,3	+ 5,7
5 3 0	12,4	-13,0
6 3 0	6,7	+ 8,7
7 3 0	17,4	-15,8
8 3 0	7,5	+ 6,4
9 3 0	21,5	+21,5
10 3 0	5,1	+ 4,8
11 3 0	12,0	-11,5
12 3 0	2,6	- 1,7
13 3 0	6,8	- 6,0
14 3 0	-	- 1,0
15 3 0	18,1	+20,8
0 4 0	13,2	-13,1
1 4 0	15,1	-15,9
2 4 0	2,5	+ 3,8
3 4 0	6,9	+ 6,1
4 4 0	8,4	+ 9,1
5 4 0	19,4	+16,8
6 4 0	-	- 1,9
7 4 0	26,7	-27,1
8 4 0	6,2	+9 ,8
9 4 0	6,6	- 9,5
10 4 0	6,3	+ 4,6
11 4 0	13,1	+11,3
12 4 0	10,5	-10,4
13 4 0	11,7	-12,9
1 5 0	2,8	+ 4,0
2 5 0	22,5	-22,6
3 5 0	19,2	-17,6
4 5 0	2,8	+ 3,1
5 5 0	--	- 0,1
6 5 0	--	- 1,1
7 5 0	--	+ 1,9
8 5 0	6,4	- 6,0
9 5 0	12,4	-10,7
10 5 0	11,6	-13,6
11 5 0	7,2	+ 6,5
0 6 0	16,9	+13,5
1 6 0	7,9	+ 6,7
2 6 0	8,9	- 6,9
3 6 0	8,7	+ 8,3
4 6 0	8,5	- 5,6
5 6 0	2,4	+ 3,0
6 6 0	13,5	-12,8
7 6 0	3,2	+ 2,7
8 6 0	9,3	- 9,6
0 0 1	72,5	+72,5
2 0 1	21,9	-19,1
4 0 1	39,5	-37,3
6 0 1	17,6	+19,5
8 0 1	13,9	-13,1
10 0 1	14,5	-17,0
12 0 1	12,2	+13,0
14 0 1	7,8	- 7,0
16 0 1	9,6	- 7,9
0 0 2	27,8	+26,2
2 0 2	15,4	-12,7
4 0 2	26,8	-26,8
6 0 2	15,6	+16,8
8 0 2	8,6	- 8,3
10 0 2	15,6	-17,7
12 0 2	8,6	+10,0
0 0 3	15,4	+16,1
2 0 8	---	+ 0,3
4 0 3	11,9	-14,0
6 0 3	11,4	+12,4
8 0 3	5,6	- 3,9
10 0 3	13,9	-11,4
0 0 4	14,1	+15,2
2 0 4	8,0	+ 9,1
4 0 4	6,2	+ 7,8
$\bar{2}$ 0 1	7,2	+ 3,0
$\bar{4}$ 0 1	7,2	- 4,0
$\bar{6}$ 0 1	28,9	+30,2
$\bar{8}$ 0 1	24,3	-24,7
$\bar{10}$ 0 1	---	- 1,1
$\bar{12}$ 0 1	37,0	+35,1
$\bar{14}$ 0 1	---	- 1,0
$\bar{16}$ 0;1	5,5	- 6,2
$\bar{2}$ 0 2	23,8	-23,6
$\bar{4}$ 0 2	4,0	- 3,8
$\bar{6}$ 0 2	21,0	+24,8
$\bar{8}$ 0 2	31,9	-31,2
$\bar{10}$ 0 2	8,7	- 6,4
$\bar{12}$ 0 2	31,5	+30,4
$\bar{14}$ 0 2	---	- 0,9
$\bar{16}$ 0 2	2,4	+ 2,4
$\bar{2}$ 0 3	25,0	-26,0
$\bar{4}$ 0 3	7,2	- 5,8
$\bar{6}$ 0 3	14,5	+16,4
$\bar{8}$ 0 3	25,5	-25,5
$\bar{10}$ 0 3	8,6	- 6,9
$\bar{12}$ 0 3	16,3	+15,7
$\bar{14}$ 0 3	8,7	- 8,0
$\bar{16}$ 0 3	4,8	+ 4,9
$\bar{2}$ 0 4	14,7	-17,7
$\bar{4}$ 0 4	3,4	- 3,4
$\bar{6}$ 0 4	6,5	+ 8,8
$\bar{8}$ 0 4	16,7	-17,7
$\bar{10}$ 0 4	---	- 0,3
$\bar{12}$ 0 4	9,6	+ 8,1

subtracting from the experimental values the contributions of C_1 and C_2. By this R was reduced to 0·13. Further adjustments and the introduction of hydrogen atoms reduced R to the final value of 0·09. The final atomic coordinates are listed in Table 1.

Estimation of accuracy

The standard deviation of the atomic coordinates was estimated by the method of Cruickshank (1949) from the relationship:

$$\sigma(x_i) = \frac{\frac{2\pi}{a_t A}(\Sigma m h_i^2 \Delta F^2)^{\frac{1}{2}}}{2p\varrho_0} .$$

The values obtained were:

$$\sigma(x) \simeq \sigma(y) \simeq 0{\cdot}008 \text{ Å for C atoms}$$

and

$$\sigma(x) \simeq \sigma(y) \simeq \sigma(z) \simeq 0{\cdot}002 \text{ Å for Cl atom.}$$

The application of Cruickshank's method to the $h0l$ reflections for the determination of $\sigma(z)$ for carbon atoms is ruled out by the overlapping of atoms which occurs in that projection. For the Cl atom, the standard deviation is only slightly influenced by the anisotropic thermal factor owing to the smallness of the effect (20% difference in the direction of maximum and minimum vibration). Values of the standard deviation for bond distances are of 0·011 Å for bonds C–C and of 0·008 Å for the bond C–Cl.

Shape of molecule

The mean plane of the molecule of *p*-dichlorobenzene was derived and a new group of atomic coordinates calculated on a set of three orthogonal axes ξ, η, ζ, with the origin at the centre of the molecule. Axes ξ and η lay in the mean plane of the molecule, the axis ζ being normal to this plane. In Table 3 values of the coordinates in Å are shown.

Table 3. *Coordinates of the atoms of the molecule of* p-*dichlorobenzene referred to the axes* ξ, η, ζ

Atom	ξ	η	ζ
Cl_1	−3·097 Å	−0·159 Å	−0·007 Å
C_1	−1·361	−0·059	+0·001
C_2	−0·761	+1·167	+0·014
C_3	+0·627	+1·235	−0·015

In Fig. 2 the projection of the molecule on the mean plane is shown; the coordinate ζ represents the displacement of the atomic positions from the mean plane. The bond lengths and bond angles calculated are listed in Table 4.

Table 4. *Intramolecular distances and bond angles*

Bond lenghts	
Cl_1–C_1	1·74 ± 0·01 Å
C_1–C_2	1·37 ± 0·01
C_2–C_3	1·39 ± 0·01
C_3–C_1'	1·39 ± 0·01

Bond angles	
Cl–C_1–C_2	120° ± 40′
Cl–C_1–C_3'	118° 30′ ± 40′
C_3'–C_1–C_2	121° 30′ ± 40′
C_1–C_2–C_3	119° 10′ ± 40′
C_2–C_3–C_1'	119° 20′ ± 40′

The bonds Cl–C_1, C_1–C_2, C_2–C_3 form angles of 0° 14′, 0° 34′ and 1° 12′ respectively with the mean plane; at a temperature of −140° C. the molecule may therefore be taken as plane. Distances C–C, within the limits of error, are equal one to the other and also to those usually found in the benzene ring (1·39 Å). It is possible that the slight differences are due to inaccurate placing of the C_1 atoms, for which it was not possible to derive corrections for the probable anisotropic thermal vibration and which are not close to the lines Cl–Cl.

It is necessary to note that if atom C_1 is assumed to lie on the line Cl–Cl rotating the bond C_1–C_3' round C_3', all distances in the benzene ring become equal to 1·39 Å and all angles become about 120°.

We are working on the refinement with experimental data obtained at room temperature.

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