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A Nuclear Quadrupole Resonance and X-Ray Study of the Crystal Structure of Pentachlorophenol

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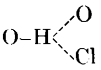
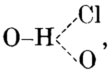
The crystal structure of the pentachlorophenol, C_6Cl_5OH, was solved by the combined application of nuclear quadrupole resonance and X-ray diffraction. The molecules are linked by chains of hydrogen-bonds with a configuration similar to that in tetrachlorohydroquinone $C_6Cl_4(OH)_2$. The nuclear quadrupole resonance of one of the ortho chlorine atoms is specially affected by the intermolecular interaction. This interaction is attributed to the proton on the OH group of the adjacent molecule, and the existence of  $\mathrm{O{-}H}\Big\langle\begin{matrix}\mathrm{O}\\ \mathrm{Cl}\end{matrix}$ bifurcated hydrogen bonds with bond lengths O–H · · · O = 2·97 Å and O–H · · · Cl = 3·28 Å is inferred.

During the phase determination, a pseudo solution was obtained, which was unusually close to the true solution. The relation between these two solutions is discussed.

Introduction

This paper is a part of the series of investigations (Dean, Pollak, Craven & Jeffrey, 1958; Chu, Jeffrey & Sakurai, 1962; Sakurai, 1962; Sakurai, Sundaralingam & Jeffrey, 1963) making use of both nuclear quadrupole resonance (n.q.r.) and X-ray diffraction for the crystal structure determination.

Four frequencies were reported by Bray & Esteva (1954) for the pure nuclear quadrupole resonance of Cl^{35} of the pentachlorophenol C_6Cl_5OH at 77 °K. Since the molecule has five chlorine nuclei, five or some multiple of five frequencies are expected if the molecule has no symmetry, and three or some multiple of three if it has mirror symmetry perpendicular to the molecular plane. But four frequencies are hard to explain. The initial objective of this work was to explore whether there is any structural reason why one frequency should disappear. It soon became clear that five frequencies exist at room temperature and those corresponding to chlorine 2 and chlorine 4 accidentally degenerate at low temperature. Both of these resonances are very similar, but the resonance corresponding to chlorine 1 and chlorine 5 have some different properties. A significant disagreement between X-ray and quadrupole result revealed that one of the ortho chlorine nuclei is largely affected by an intermolecular interaction. This intermolecular effect is qualitatively attributed to the proton near this chlorine nucleus, and the evidence of bifurcated hydrogen bond between  $\mathrm{O{-}H}\Big\langle\begin{matrix}\mathrm{Cl}\\ \mathrm{O}\end{matrix}$, which was suggested previously for tetrachlorohydroquinone (Sakurai, 1962) is further substantiated.

Crystal data

The crystals are monoclinic and the unit cell dimensions are

$$a = 29{\cdot}11 \pm 0{\cdot}03,\quad b = 4{\cdot}930 \pm 0{\cdot}005,\quad c = 12{\cdot}09 \pm 0{\cdot}02\ \text{Å};$$
$$\beta = 93^\circ\ 38' \pm 4',\quad V = 1732 \pm 5\ \text{Å}^3,\quad Z = 8;$$
$$D_m = 2{\cdot}01\ \text{g.cm.}^{-3},\quad D_x = 2{\cdot}043 \pm 0{\cdot}006\ \text{g.cm.}^{-3}.$$

The systematic extinctions are $h+k=$ odd for (hkl) and $l=$ odd for $(h0l)$ reflections. Therefore the space group is either $C2/c$ or Cc. The number of the molecules in an asymmetric unit is one if the space group is $C2/c$ and two if it is Cc. Since at room temperature five n.q.r. frequencies of Cl^{35} were observed, there is one molecule in the asymmetric unit, and by the combination of techniques the space group is uniquely determined to be $C2/c$.

Experimental

Fisher's highest purity grade sample was purified by recrystallization from alcoholic solution.

The n.q.r. measurements were made on a spectrometer described by Dean (1960). A single crystal for n.q.r. work was grown by slow evaporation of alcoholic solution. The crystal had parallelepiped shape elongated along the b axis, and was surrounded by clear cleavage faces $\{100\}$ and $\{10\bar{1}\}$. The dimensions of the crystal were $25 \times 10 \times 6$ mm.³ and the oscillator coil was wound directly around it. Five pure quadrupole resonance frequencies were observed at room temperature. Zeeman non-splitting loci for each frequency was observed under weak magnetic field. From the arrangement of symmetrical configuration of these loci, the direction of b axis could be determined accurately. Those of a and c axes were determined with respect to the largest cleavage plane $\{10\bar{1}\}$.

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Table 1. *Frequencies and asymmetry parameters of quadrupole resonance*

	Present results (room temp.)			Bray & Esteva (77 °K.)	
	Frequency	Intensity	Asymmetry parameter	Frequency	Intensity (signal to noise ratio)
ν_3	38·02	strong	$0{\cdot}167 \pm 0{\cdot}010$	38·5794	6
ν_4	37·75	medium	$0{\cdot}185 \pm 0{\cdot}018$	38·1915	7–8
ν_2	37·71	medium	$0{\cdot}164 \pm 0{\cdot}013$		
ν_1	36·98	medium	$0{\cdot}163 \pm 0{\cdot}017$	37·3750	4
ν_5	36·67	weak	$0{\cdot}100 \pm 0{\cdot}007$	37·1292	2

The intensity data for the X-ray analysis were obtained from multiple film Weissenberg photographs with Cu $K\alpha$ radiation of the zero to the 3rd layer of the b axis. In order to reduce the absorption error, a crystal with an approximately rectangular cross section, 0·06 mm. × 0·05 mm. was used. The effect of α_1 and α_2 resolution of the X-ray spectrum was corrected by the method described in the previous paper (Sakurai, 1962) and the correlation factors between different layers were obtained by double slit Weissenberg method (Stadler, 1950). The observed intensities were reduced to relative structure amplitudes using an IBM 650 L.p. correction program of Shiono (1960*b*). The observed data consisted of 1060 reflections, which are about 55% of the total reflections in the limiting sphere.

Determination of the structure

Comparing the observed pure quadrupole resonance frequencies and their intensities with those reported by Bray & Esteva (1954), it soon became clear that the frequencies ν_2 and ν_4 accidentally coincide at low temperature (Table 1).

From the general trend of the frequency shift due to the number of the ortho chlorine neighbors in multi chlorobenzene derivatives (Bray, Burnes & Bersohn, 1956) and the shape of the molecule, the highest frequency is assigned to Cl_3, the second and third ones to Cl_2 and Cl_4 and lower two frequencies to Cl_1 and Cl_5 (Fig. 1). These assignments were definitely confirmed in the later stage of the analysis by comparison with the X-ray results. For convenience of notation, the corresponding chlorine position is used as the subscript for the frequency throughout the paper.

Four Zeeman non-splitting loci exist for each frequency and all 20 loci were observed. Among them, two loci for Cl_3 related by mirror symmetry overlap each other as shown in Fig. 2. The others are well resolved. The σ bond direction for each frequency was obtained by least square method and b axis of

Table 2. *The relative orientations of the* Cl σ *bonds*

	n.q.r.	X-ray
b axis and $Cl_1\sigma$ bond	54·5	54·3
b axis and $Cl_2\sigma$ bond	48·4	48·9
b axis and $Cl_3\sigma$ bond	87·0	87·4
b axis and $Cl_4\sigma$ bond	54·2	53·9
b axis and $Cl_5\sigma$ bond	50·1	49·6
$Cl_1\sigma$ bond and $Cl_2\sigma$ bond	61·5	61·5
$Cl_2\sigma$ bond and $Cl_3\sigma$ bond	59·8	59·8
$Cl_3\sigma$ bond and $Cl_4\sigma$ bond	60·3	60·5
$Cl_4\sigma$ bond and $Cl_5\sigma$ bond	61·5	59·5

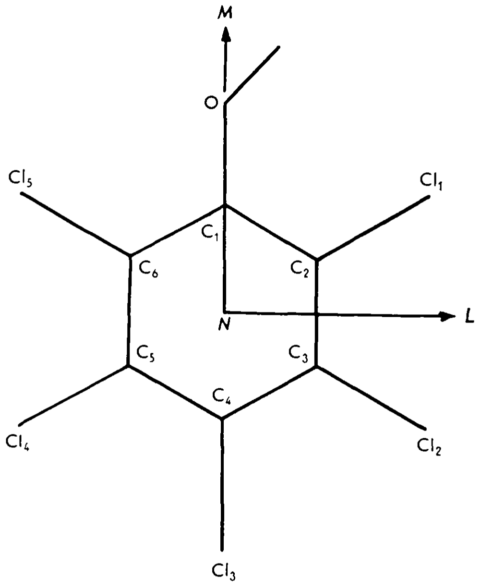


Fig. 1. The molecular axes.
N is perpendicular to the plane of the paper.

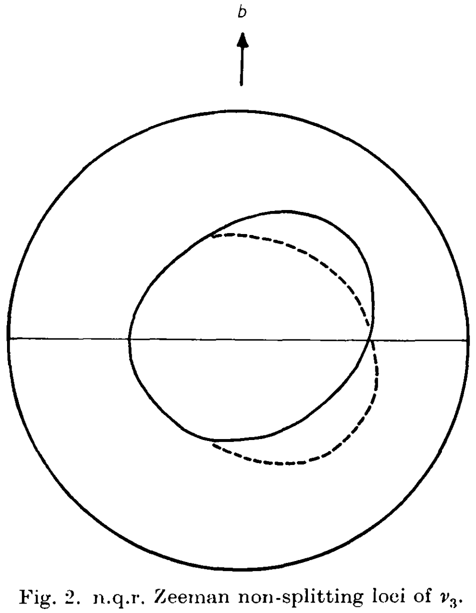


Fig. 2. n.q.r. Zeeman non-splitting loci of ν_3.

the crystal is also determined from the disposition of the loci. The relative orientations of these bonds are shown in Table 2.

The standard error of these relative orientations is 0·2°. The asymmetry parameters were obtained graphically and are shown in Table 1.

The molecular axes are defined as shown in Fig. 1. These directions were related to the crystal axes in the following way. First a best fit plane through the five C–Cl bonds was obtained by least square method and the normal to this plane was taken as the molecular axis N. Axis M was taken perpendicularly to N in the plane containing N and Cl_3 bond, and L was taken perpendicularly to N and M. Thus the direction cosines between the molecular axes and the crystal axes were obtained. The deviations of the C–Cl bonds from the plane of the molecule are small as shown in Table 3. Therefore the molecule was assumed to be planar and the coordinates of atoms in the crystal with respect to the origin of the molecule were calculated by the assumption that the bond angles are all 120° and the C–Cl, C–C and C–O distances are 1·74, 1·39 and 1·35 Å respectively. These results are shown in Tables 4 and 5.

Table 3. *Deviation of the* C–Cl *bonds from the plane of the molecule*

	n.q.r.	X-ray
Cl_1	0·4°	−1·5°
Cl_2	−1·3	−1·2
Cl_3	0·7	1·9
Cl_4	−1·3	0·8
Cl_5	0·2	0·1

Table 4. *Approximate direction cosines between molecular axes and crystal axes deduced from n.q.r. data*

	a'*	b	c
L	0·128	−0·718	−0·680
M	−0·989	−0·060	−0·130
N	0·052	0·693	−0·722

* For convenience of calculation, orthogonal axes a', b and c were used, where a' is perpendicular to bc plane.

Table 5. *Approximate atomic coordinates with respect to the molecular origin*

	x	y	z
Cl_1	0·064	−0·38	−0·124
Cl_2	−0·042	−0·41	−0·176
Cl_3	−0·106	−0·09	−0·052
Cl_4	−0·064	0·38	0·124
Cl_5	0·042	0·41	0·176
C_2	0·029	−0·17	−0·055
C_3	−0·019	−0·18	−0·078
C_4	−0·047	−0·04	−0·023
C_5	−0·029	0·17	0·055
C_6	0·019	0·18	0·078
C_1	0·047	0·04	0·023
O	0·093	0·08	0·045

The coordinates of the molecular origin were determined from the (010) projection. In this projection, the structure factor expression has the form

$$F=A\cos 2\pi(hX+lZ)+B\sin 2\pi(hX+lZ)\ ,$$

where X, Z are the coordinates of the origin of the molecule, and A, B are real and imaginary part of the molecular structure factor, which are readily calculated from the parameter values in Table 5. All reflections with small $|F_o|$ values were selected and A, B were calculated for these reflections. Then X and Z were obtained from the condition

$$A\cos 2\pi(hX+lZ)+B\sin 2\pi(hX+lZ)\simeq 0\ .$$

The two-dimensional structure was refined by ordinary Fourier method and after two cycles the agreement index, R, was reduced to 13%. In order to determine the coordinate of the molecular origin Y, reflections with small $|F_o|$ values were again selected from the three-dimensional data and the condition to determine Y is simply,

$$C\cos 2\pi kY+D\sin 2\pi kY\simeq 0\ ,$$

where C and D are calculated from two-dimensional structure and y coordinates in Table 5. The first approximate value of Y was 0·255. This value gave an R factor of 29%. The chlorine atoms were refined by differential Fourier method and the new carbon coordinates were readily obtained from the parameters in Table 5. After one cycle of refinement the R factor was reduced to 18%. Finally a differential Fourier refinement was computed for all atoms and an R factor of 14% was obtained, excluding non-observed reflections. In all these calculations isotropic temperature factors were used. In this way, the phase problem was solved rapidly and straight forwardly except for one pseudo solution which appeared in the initial stage of the two-dimensional analysis. This pseudo solution has a particular interest in relation to the general problem of phase determination and will be discussed later. The atomic coordinates and isotropic temperature factors are shown in Table 6.

Table 6. *Atomic coordinates and isotropic temperature factors in unit cell fractions*

	x	y	z	B
Cl_1	0·20067	−0·1068	0·0497	4·0
Cl_2	0·09574	−0·1544	−0·0132	4·0
Cl_3	0·02768	0·2183	0·0996	4·0
Cl_4	0·06470	0·6168	0·2803	4·0
Cl_5	0·16953	0·6583	0·3419	3·7
C_1	0·1793	0·277	0·1905	3·0
C_2	0·1624	0·096	0·1116	3·0
C_3	0·1163	0·074	0·0838	3·0
C_4	0·0862	0·234	0·1362	3·0
C_5	0·1009	0·416	0·2158	3·0
C_6	0·1489	0·437	0·2448	3·0
O	0·2243	0·288	0·2168	3·7

Standard deviation of the atomic coordinates

	a	b	c
Cl	0·003 Å	0·005 Å	0·004 Å
C	0·011	0·014	0·014
O	0·009	0·012	0·012

Table 7. *Observed and calculated structure factors*

(h	k	l)	$\|F_o\|$	F_c
4			144.0	144.1-
6			2.4	6.0
8			196.2	209.2-
10			94.6	101.8
12			73.5	75.2
14			70.5	68.9-
16			115.6	108.7-
18			15.3	13.2
20			33.2	18.8-
22			68.7	57.7-
24			32.3	23.0-
26			57.4	52.4-
28			13.4	16.8-
30			65.9	68.1
32			26.0	16.8
34			41.2	28.6
36			22.9	8.1
		2	52.2	46.9-
2		2	66.5	76.6-
4		2	24.4	15.8-
6		2	113.4	111.0-
8		2	88.4	92.8
10		2	39.2	35.5
12		2	165.7	179.0-
14		2	95.9	76.9-
16		2	137.4	133.7-
18		2	83.6	65.0-
20		2	123.2	118.0
22		2	5.7	.1-
24		2	92.6	90.2
26		2	19.2	7.3
28		2	37.7	50.3-
30		2	37.4	35.5
32		2	17.6	16.6
34		2	22.8	11.4
- 2		2	99.9	105.8
- 4		2	25.9	30.5
- 6		2	90.0	85.3
- 8		2	44.8	44.9
-10		2	338.8	375.5
-12		2	33.9	28.0
-14		2	67.1	70.5-
-16		2	4.5	7.4
-18		2	154.3	147.7-
-20		2	33.5	38.7
-22		2	5.6	1.2-
-24		2	13.2	16.9-
-26		2	10.4	11.5-
-28		2	26.9	27.6-
-30		2	25.8	15.5-
-32		2	31.7	25.6-
		4	61.6	56.8
2		4	129.3	132.9-
4		4	18.6	19.7-
6		4	295.6	325.3-
8		4	114.4	119.1-
10		4	92.4	94.2
12		4	42.1	30.5-
14		4	146.2	146.1
16		4	11.4	13.7-
18		4	5.4	12.0-
20		4	40.5	29.5
22		4	59.6	49.6
24		4	13.5	7.0
26		4	23.2	29.6-
28		4	54.5	50.2
30		4	12.9	11.7
32		4	12.1	13.6
- 2		4	104.8	98.8
- 4		4	92.5	94.2-
- 6		4	65.9	71.5-
- 8		4	80.0	79.7
-10		4	37.4	44.1
-12		4	9.4	.3-
-14		4	24.9	26.5
-16		4	87.4	65.8
-18		4	33.0	35.5
-20		4	159.7	163.9
-22		4	10.0	9.1
-24		4	124.7	136.9-
-26		4	6.0	9.9
-28		4	42.0	45.2-
-30		4	5.6	12.3
-32		4	24.7	28.2
-34		4	27.9	31.3-
		6	18.5	23.2-
2		6	32.5	34.5-
4		6	120.4	116.7
6		6	31.5	29.5-
8		6	4.6	12.6
10		6	21.8	13.7
12		6	88.9	77.2
14		6	5.4	8.8-
16		6	5.6	7.5-
18		6	58.7	57.9
20		6	13.4	14.2
22		6	57.5	56.8
24		6	32.6	31.3
26		6	59.4	63.2-
28		6	31.2	20.4-
30		6	25.7	15.4-
32		6	31.5	19.5-
- 2		6	73.1	75.5-
- 4		6	264.8	292.2-
- 6		6	25.5	20.0
- 8		6	88.2	87.3-
-10		6	92.0	82.8
-12		6	162.9	149.6
-14		6	106.6	96.8-
-16		6	34.1	28.9-
-18		6	9.8	18.3
-20		6	8.3	2.6
-22		6	60.3	75.5
-24		6	42.9	45.9
-26		6	5.9	19.0-
-28		6	5.6	10.5
-30		6	31.1	37.9
-32		6	4.5	3.4-
-34		6	34.3	34.2-
		8	22.8	21.9
2		8	136.3	132.0
4		8	74.0	71.1-
6		8	75.7	64.6-
8		8	79.6	82.4
10		8	21.9	22.2
12		8	114.8	120.3
14		8	94.1	98.3
16		8	119.4	123.0-
18		8	27.1	26.5-
20		8	5.9	2.7-
22		8	18.1	22.3-
24		8	5.3	8.3
26		8	24.7	16.6-
28		8	31.0	17.7-
30		8	12.2	9.0-
- 2		8	16.1	3.7-
- 4		8	8.8	7.3-
- 6		8	5.2	8.9-
- 8		8	11.8	18.1-
-10		8	62.1	69.8-
-12		8	30.7	28.5-
-14		8	126.3	122.7-
-16		8	26.4	13.4
-18		8	26.9	17.3
-20		8	19.2	15.4
-22		8	57.0	63.2
-24		8	31.9	32.1-
		10	10.2	18.7
2		10	83.7	90.9
4		10	56.5	69.9
6		10	46.5	41.0-
8		10	6.0	12.4
10		10	6.0	13.0-
12		10	6.0	4.1-
14		10	42.2	57.1-
16		10	18.4	13.2-
18		10	5.5	9.0
20		10	15.6	15.5-
22		10	24.1	23.6
24		10	30.8	31.7-
26		10	20.0	20.0-
- 2		10	52.7	59.3
- 4		10	61.9	50.4-
- 6		10	56.3	46.9-
- 8		10	62.7	60.2
-10		10	6.0	9.6
-12		10	6.0	4.7-
-14		10	6.0	.2
-16		10	33.0	37.9-
-18		10	10.2	18.2-
-20		10	34.0	30.9-
-22		10	13.3	14.4-
-24		10	35.0	34.1-
-26		10	11.9	8.2
-28		10	29.7	20.8
		12	5.9	2.6-
2		12	5.9	4.0
4		12	18.6	26.0-
6		12	5.8	.8-
8		12	36.0	39.9-
10		12	5.5	1.5-
12		12	29.1	26.1
14		12	27.5	31.9-
16		12	4.6	3.9-
18		12	26.9	25.6-
20		12	27.2	28.2-
- 2		12	5.9	15.1
- 4		12	32.6	19.6-
- 6		12	41.0	55.8
- 8		12	85.9	97.3
-10		12	31.8	25.4-
-12		12	12.7	10.6
-14		12	31.7	30.7-
-16		12	45.0	36.7-
-18		12	52.0	47.3
		14	14.2	10.4
2		14	46.7	40.3
4		14	32.1	33.1-
6		14	22.2	25.4-
8		14	18.8	20.2-
10		14	24.8	28.0-
12		14	22.3	18.2
- 2		14	27.4	29.3-
- 4		14	9.5	5.0
- 6		14	51.5	49.6-
- 8		14	4.5	8.7
-10		14	42.0	48.6
-12		14	4.2	3.0
-14		14	3.8	3.5
3	1		39.5	28.8-
5	1		45.2	37.0
7	1		20.8	19.1-
9	1		144.1	149.1
11	1		44.6	42.5
13	1		99.0	105.3-
15	1		3.0	.7-
17	1		103.2	90.9-
19	1		6.7	3.8
21	1		25.0	30.3
23	1		7.5	3.6-
25	1		53.1	45.9
27	1		19.2	24.3-
29	1		13.1	17.7-
1	1	1	48.8	55.0-
3	1	1	64.9	60.7-
5	1	1	32.4	27.6-
7	1	1	159.7	155.8-
9	1	1	269.1	268.5-
11	1	1	76.9	74.6
13	1	1	30.7	32.7-
15	1	1	80.7	79.8
17	1	1	73.7	68.5
19	1	1	39.6	42.0-
21	1	1	39.1	24.7
23	1	1	41.0	35.6
25	1	1	42.2	34.7
27	1	1	7.8	9.8-
29	1	1	37.7	23.7
31	1	1	19.7	17.4
- 1	1	1	29.8	29.4-
- 3	1	1	16.2	5.6
- 5	1	1	5.0	5.3-
- 7	1	1	110.6	120.5
- 9	1	1	4.1	7.5
-11	1	1	15.5	18.8-
-13	1	1	70.1	72.6
-15	1	1	94.5	80.4
-17	1	1	66.6	69.9
-19	1	1	128.7	125.2
-21	1	1	72.9	75.9-
-23	1	1	51.4	52.6-
-25	1	1	11.0	11.0-
-27	1	1	53.5	47.9-
-29	1	1	26.4	37.1
-33	1	1	30.1	30.0-
1	1	2	94.2	84.2
3	1	2	128.5	134.5-
5	1	2	3.6	4.7
7	1	2	200.1	198.3-
9	1	2	21.6	15.3
11	1	2	47.6	51.1
13	1	2	5.4	1.2-
15	1	2	28.6	22.2
17	1	2	15.8	18.8-
19	1	2	6.9	7.2
21	1	2	7.3	13.3-
23	1	2	7.7	7.1
25	1	2	22.2	19.3-
27	1	2	13.5	21.1-
29	1	2	43.4	39.4
31	1	2	15.2	10.0
33	1	2	17.7	14.3
- 1	1	2	306.8	345.1
- 3	1	2	107.4	104.5-
- 5	1	2	70.9	67.1-
- 7	1	2	3.9	3.6-
- 9	1	2	20.9	21.0-
-11	1	2	26.0	32.9
-13	1	2	5.3	8.8
-15	1	2	5.8	1.5-
-17	1	2	19.9	16.6-
-19	1	2	68.9	71.5
-21	1	2	20.4	26.1
-23	1	2	77.2	84.7-
-25	1	2	7.8	9.3-
-27	1	2	22.2	20.4-
-29	1	2	7.5	.8-
-31	1	2	38.6	35.4
-33	1	2	10.7	5.9-
1	1	3	111.4	106.6
3	1	3	58.4	60.0-
5	1	3	82.7	79.1
7	1	3	24.1	25.5
9	1	3	54.8	51.7-
11	1	3	5.3	5.8-
13	1	3	123.4	106.5
15	1	3	59.7	50.7
17	1	3	14.9	24.1-
19	1	3	59.3	47.8
21	1	3	40.5	29.5
23	1	3	37.3	29.3
25	1	3	42.4	40.9
27	1	3	25.5	23.9-
29	1	3	49.3	41.4-
33	1	3	38.6	25.3-
- 1	1	3	372.8	382.7-
- 3	1	3	271.5	262.4-
- 5	1	3	90.0	79.8
- 7	1	3	82.4	81.4-
- 9	1	3	141.4	158.9
-11	1	3	29.7	20.6
-13	1	3	83.7	94.7-
-15	1	3	10.4	9.6
-17	1	3	57.9	64.6
-19	1	3	16.9	28.3
-21	1	3	55.5	57.3
-23	1	3	25.4	22.7
-25	1	3	7.8	10.4-
-27	1	3	32.2	33.2
-29	1	3	21.2	33.6
1	1	4	67.6	93.2-
3	1	4	30.2	31.4
5	1	4	41.8	38.7
7	1	4	4.9	3.2-
9	1	4	36.1	44.3
11	1	4	38.7	45.2-
13	1	4	6.1	12.2-
15	1	4	35.3	30.2-
17	1	4	19.7	24.7-
19	1	4	43.0	43.9
21	1	4	7.6	4.7
23	1	4	53.3	49.3
25	1	4	13.5	14.9
27	1	4	46.5	46.1-
- 1	1	4	4.2	2.9
- 3	1	4	95.5	85.2-
- 5	1	4	4.5	.5-
- 7	1	4	36.0	26.4-
- 9	1	4	34.5	29.7
-11	1	4	105.6	179.4
-13	1	4	40.1	50.0-
-15	1	4	20.8	25.4-
-17	1	4	16.4	12.0-
-19	1	4	48.3	47.8-
-21	1	4	35.9	45.0
-23	1	4	13.4	21.2
-25	1	4	7.8	5.6-
-27	1	4	7.7	2.8-
-29	1	4	7.3	7.1
-31	1	4	6.7	.1
-33	1	4	17.6	21.9-
1	1	5	28.8	22.0-
3	1	5	144.2	130.4
5	1	5	30.6	27.2
7	1	5	85.3	79.8-
9	1	5	55.8	54.9
11	1	5	93.3	77.0
13	1	5	60.4	57.5
15	1	5	144.5	131.6
17	1	5	42.5	40.5-
19	1	5	77.2	72.0-
21	1	5	7.8	3.6
23	1	5	53.3	50.6-
25	1	5	13.3	17.2
27	1	5	7.2	.6-
29	1	5	43.5	29.0-
31	1	5	23.6	16.5-
- 1	1	5	16.2	15.5
- 3	1	5	44.3	42.3-
- 5	1	5	7.2	13.8-
- 7	1	5	69.4	64.2-
- 9	1	5	49.7	43.9-
-11	1	5	84.4	104.5-
-13	1	5	96.8	115.3-
-15	1	5	49.9	53.6
-17	1	5	9.9	19.2-
-19	1	5	49.9	58.2
-21	1	5	18.7	21.5
-23	1	5	11.0	13.2-
-25	1	5	11.1	20.1
-27	1	5	7.6	4.6
-29	1	5	7.1	20.2
-31	1	5	19.4	18.0
-33	1	5	16.5	17.2
1	1	6	7.8	2.4
3	1	6	66.5	52.6
5	1	6	116.5	113.3-
7	1	6	64.8	60.2-
9	1	6	64.3	57.2
11	1	6	6.6	8.3-
13	1	6	122.6	108.8
15	1	6	55.0	24.9
17	1	6	77.0	76.0-
- 1	1	6	9.5	17.6
- 3	1	6	9.6	15.2
- 5	1	6	8.0	19.3-
- 7	1	6	5.6	4.8
- 9	1	6	29.1	26.8-
-11	1	6	6.3	.8-
-13	1	6	50.2	51.8-
-15	1	6	6.9	1.7-
-17	1	6	35.0	33.4
-19	1	6	7.5	9.7
-23	1	6	19.2	27.9-
-25	1	6	25.7	41.2-
1	1	7	62.8	67.9
3	1	7	52.2	52.6
5	1	7	161.5	151.9
7	1	7	31.8	20.6-
9	1	7	19.4	12.7-
11	1	7	7.1	1.2-
13	1	7	20.9	27.1-
15	1	7	13.2	13.8-
17	1	7	45.5	38.8-
19	1	7	13.6	5.3-
21	1	7	45.4	33.3-
23	1	7	16.8	17.5
25	1	7	12.2	7.7-
27	1	7	37.0	33.2-
- 1	1	7	35.8	34.0
- 3	1	7	91.0	72.8-
- 5	1	7	6.2	9.1
- 7	1	7	89.5	80.9
- 9	1	7	31.6	23.4-
-11	1	7	32.7	37.2-
-13	1	7	7.0	13.7-
-15	1	7	20.8	33.3-
-17	1	7	21.4	26.6-
-19	1	7	13.4	21.2-
-21	1	7	37.7	50.2-
-23	1	7	42.0	55.0-
-25	1	7	46.7	56.4
-27	1	7	14.2	14.6
-29	1	7	15.8	15.3
-31	1	7	16.7	21.3
-33	1	7	22.0	27.4-
1	1	8	9.6	12.9-
3	1	8	87.0	80.1
5	1	8	9.9	9.9
7	1	8	23.7	14.2-
15	1	8	42.2	41.8-
17	1	8	13.6	21.5
19	1	8	7.7	12.0
23	1	8	15.8	28.6
25	1	8	37.6	30.0-
- 1	1	8	36.4	26.4
- 3	1	8	46.0	43.5-
- 5	1	8	89.8	79.6-
- 7	1	8	37.5	28.3
- 9	1	8	17.4	14.7-
-11	1	8	42.5	40.0
-13	1	8	35.9	32.6
-15	1	8	36.7	42.5-
-17	1	8	7.8	5.1-
-19	1	8	19.2	20.8-
-21	1	8	7.8	5.9-
-31	1	8	20.0	26.8
1	1	9	7.3	9.1-
3	1	9	7.4	8.9-
5	1	9	7.5	2.0-
7	1	9	7.6	7.3-
9	1	9	37.0	32.1-
11	1	9	45.6	40.5-
13	1	9	22.2	17.4
15	1	9	26.0	28.0-
17	1	9	13.3	10.8-
19	1	9	12.9	13.7-
21	1	9	47.6	43.7-
23	1	9	11.1	3.6
25	1	9	40.7	32.4
- 1	1	9	17.9	20.4
- 3	1	9	17.9	9.4-
- 5	1	9	129.8	132.5
- 7	1	9	50.5	47.6
- 9	1	9	10.6	.2
-11	1	9	17.1	19.5
-13	1	9	58.7	78.6-
-15	1	9	7.8	7.5
-17	1	9	45.9	47.0
-19	1	9	7.7	16.4-
-25	1	9	27.7	38.6-
-31	1	9	15.3	10.2-
1	1	10	31.9	27.8
3	1	10	7.7	6.4-
5	1	10	42.1	39.9-
7	1	10	7.8	16.5
9	1	10	13.6	15.3-
11	1	10	37.6	31.0
13	1	10	45.2	45.5
15	1	10	40.8	45.1-
17	1	10	16.2	15.0-
- 1	1	10	7.7	1.5
- 3	1	10	13.3	9.6-
- 5	1	10	7.7	5.5
- 7	1	10	74.7	68.5
- 9	1	10	13.5	18.5-
-11	1	10	10.6	22.7-
-13	1	10	7.6	12.4-
-15	1	10	42.1	48.5-
-17	1	10	13.8	29.6
1	1	11	42.4	34.9-
3	1	11	59.3	56.2
5	1	11	7.8	11.3-
7	1	11	41.9	45.3-
9	1	11	13.3	21.6-
11	1	11	53.3	63.7-
- 1	1	11	45.9	37.9-
- 3	1	11	7.3	.7
- 5	1	11	42.3	31.5-
- 7	1	11	45.0	41.9
- 9	1	11	25.9	27.9
-11	1	11	7.7	13.2
-13	1	11	7.6	9.7
-15	1	11	34.4	41.7
-23	1	11	29.6	30.1-
1	1	12	33.2	28.0
3	1	12	37.0	55.0
5	1	12	37.4	22.2-
- 1	1	12	7.0	7.2-
- 3	1	12	13.2	16.3
- 5	1	12	55.9	40.2-
- 7	1	12	10.7	15.0-
- 9	1	12	42.5	43.5
1	1	13	45.7	44.8-
13	1	13	22.0	23.6
- 7	1	13	26.5	14.6
- 7	1	14	17.3	19.3
- 9	1	14	16.7	30.1
-11	1	14	15.9	14.7-

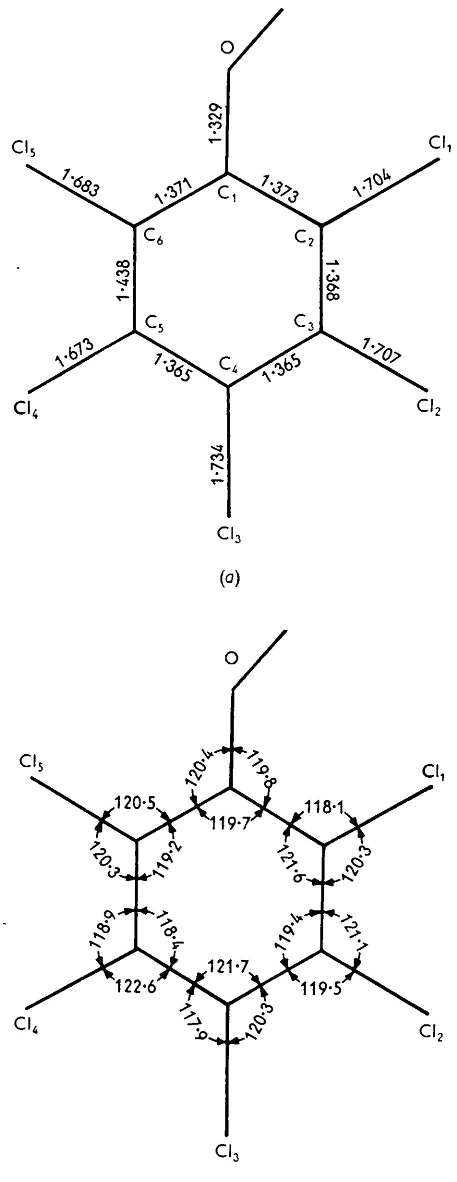
Table 7 (*cont.*)

h	k	l	$\lvert F_o\rvert$	F_c
2	2		26.9	39.9-
4	2		59.5	65.0-
6	2		16.1	13.5-
8	2		29.0	19.3
10	2		19.0	13.1-
12	2		37.6	32.6-
14	2		52.3	60.2
16	2		63.8	69.1
18	2		21.2	21.7
20	2		73.1	67.7
22	2		19.3	25.9-
24	2		8.0	2.0
26	2		15.9	25.2
32	2		17.4	10.7-
	2	1	83.8	104.6-
2	2	1	47.9	44.9
4	2	1	23.9	20.6-
6	2	1	32.1	33.8
8	2	1	10.9	20.4-
10	2	1	5.0	5.4
12	2	1	13.7	14.0-
14	2	1	5.1	5.2
16	2	1	16.3	19.0-
18	2	1	88.1	93.5-
20	2	1	52.1	49.0
22	2	1	68.5	68.5
24	2	1	24.1	13.6
26	2	1	54.6	47.4
28	2	1	40.2	40.3-
30	2	1	23.1	22.4-
32	2	1	14.8	12.0
-2	2	1	178.9	193.7-
-4	2	1	77.5	79.0
-6	2	1	49.4	56.1-
-8	2	1	164.7	189.8
-10	2	1	130.6	143.5
-12	2	1	104.2	110.5-
-14	2	1	12.1	10.8
-16	2	1	49.7	47.0-
-18	2	1	14.1	1.3-
-20	2	1	56.9	59.2
-22	2	1	15.7	7.9
-24	2	1	24.1	30.8-
-26	2	1	8.0	2.5
-28	2	1	27.7	38.0
-30	2	1	25.5	26.6-
-32	2	1	27.1	27.0-
	2	2	3.2*	.5
2	2	2	78.3	84.6-
4	2	2	100.1	104.3
6	2	2	89.7	92.5
8	2	2	4.8	1.8-
10	2	2	45.9	56.6
12	2	2	25.4	15.3
14	2	2	47.8	41.1
16	2	2	51.6	58.1
18	2	2	50.1	35.1
20	2	2	66.7	61.3-
22	2	2	7.9	6.7-
24	2	2	8.0	8.9
26	2	2	23.7	19.1-
28	2	2	7.4	4.5-
30	2	2	29.5	21.8-
32	2	2	36.7	28.2-
-2	2	2	76.4	97.7-
-4	2	2	29.2	39.1-
-6	2	2	56.9	49.9-
-8	2	2	49.3	47.7-
-10	2	2	38.8	47.3-
-12	2	2	34.8	35.5-
-14	2	2	12.3	24.1-
-16	2	2	6.6	4.7-
-18	2	2	17.5	19.6
-20	2	2	7.5	8.9
-22	2	2	19.3	23.1
-24	2	2	24.1	24.5
-26	2	2	42.2	38.2
	2	3	26.1	20.9-
2	2	3	10.3	13.9-
4	2	3	84.5	80.0
6	2	3	51.2	55.2-
8	2	3	182.9	187.7-
10	2	3	65.3	64.2
12	2	3	37.9	28.8
14	2	3	70.4	67.8
16	2	3	130.5	135.0
18	2	3	86.2	86.1-
20	2	3	19.2	23.1-
22	2	3	8.0	6.6
24	2	3	8.0	10.1-
26	2	3	19.0	17.1
-2	2	3	4.1	6.4-
-4	2	3	29.6	23.2
-6	2	3	24.5	22.8-
-8	2	3	21.9	13.5-
-10	2	3	44.3	46.4-
-12	2	3	102.9	107.4-
-14	2	3	73.5	76.7
-16	2	3	29.9	29.5
-18	2	3	55.2	59.6
-20	2	3	66.6	70.5
-22	2	3	60.1	66.8-
-24	2	3	8.5	2.6
-26	2	3	19.4	22.3-
-28	2	3	15.1	5.7-
-30	2	3	40.3	37.6
	2	4	46.5	57.6
2	2	4	33.5	33.6
4	2	4	49.4	48.2
6	2	4	40.7	45.2
8	2	4	49.7	48.6
10	2	4	15.0	8.3-
12	2	4	19.5	21.3
14	2	4	17.0	8.3
16	2	4	14.7	17.9-
18	2	4	52.9	41.8-
20	2	4	23.9	17.1-
22	2	4	42.5	37.5-
24	2	4	19.4	10.2-
-2	2	4	55.4	68.9
-4	2	4	12.1	19.2-
-6	2	4	45.0	45.8
-8	2	4	80.9	85.5-
-10	2	4	36.2	36.4-
-12	2	4	27.3	17.2-
-14	2	4	41.2	42.2-
-16	2	4	21.3	22.9-
-18	2	4	31.8	31.8-
-28	2	4	18.1	23.3
	2	5	78.9	75.9
2	2	5	39.2	33.0
4	2	5	61.0	65.6
6	2	5	121.0	116.4
8	2	5	71.6	62.8-
10	2	5	16.2	7.6-
12	2	5	25.1	18.6
14	2	5	31.9	26.5
16	2	5	47.2	44.0-
18	2	5	19.4	8.1-
20	2	5	29.0	30.4
22	2	5	8.0	6.2-
24	2	5	32.9	38.1
26	2	5	24.1	16.3-
28	2	5	45.9	42.6-
30	2	5	16.7	3.1-
-2	2	5	229.9	249.0-
-4	2	5	64.3	60.1-
-6	2	5	100.3	89.8
-8	2	5	12.0	11.4-
-10	2	5	61.4	51.4
-12	2	5	13.5	17.1-
-14	2	5	53.2	54.6-
-22	2	5	24.1	26.3-
-24	2	5	34.3	32.0
-26	2	5	23.0	19.8
-28	2	5	23.7	20.4
-30	2	5	39.4	34.3
-32	2	5	40.4	38.9-
	2	6	46.4	33.9-
2	2	6	18.6	23.9
4	2	6	29.2	23.4
6	2	6	13.1	2.4
8	2	6	16.7	20.7
10	2	6	21.0	30.0-
12	2	6	78.7	79.4-
14	2	6	7.6	7.7-
16	2	6	48.7	39.3-
18	2	6	19.7	2.2-
20	2	6	19.6	3.1-
30	2	6	14.4	9.2
-2	2	6	46.4	55.0
-4	2	6	114.9	124.2
-14	2	6	14.0	9.8
-16	2	6	27.7	19.6
-18	2	6	54.2	56.5-
-20	2	6	24.1	39.4-
-22	2	6	5.0	8.9-
-24	2	6	23.5	27.9-
	2	7	13.5	22.5
2	2	7	6.3	.2
4	2	7	30.4	24.4
6	2	7	49.0	47.9-
8	2	7	7.3	1.5
10	2	7	7.5	13.5
12	2	7	7.7	2.2
14	2	7	68.8	67.4
16	2	7	19.7	18.2-
18	2	7	35.0	37.6-
20	2	7	15.7	14.1-
22	2	7	56.8	56.9-
24	2	7	20.9	21.0
26	2	7	29.8	27.9
-2	2	7	16.6	7.6-
-4	2	7	66.3	59.6
-6	2	7	73.9	70.0
-8	2	7	53.7	48.8-
-10	2	7	17.9	12.3
-12	2	7	117.9	107.4-
-14	2	7	47.7	45.5-
-16	2	7	68.7	67.5
-18	2	7	8.0	8.0-
-20	2	7	24.1	20.0
-22	2	7	7.9	8.5-
-24	2	7	22.7	25.8-
	2	8	14.5	16.4-
2	2	8	50.9	45.7-
4	2	8	14.5	.9
6	2	8	7.6	21.7-
8	2	8	28.0	30.2-
10	2	8	48.7	43.3-
12	2	8	8.0	8.0-
14	2	8	16.1	18.7-
16	2	8	16.0	14.8
22	2	8	14.0	17.1
26	2	8	13.2	14.2
28	2	8	21.2	24.2
-2	2	8	7.3	.3-
-4	2	8	7.4	6.2-
-6	2	8	92.0	81.4
-8	2	8	15.2	21.7
-10	2	8	7.7	5.3-
-12	2	8	10.2	23.9
-14	2	8	15.9	30.9
	2	9	15.6	7.7-
2	2	9	7.8	4.5
4	2	9	102.8	110.8
6	2	9	15.9	15.7-
8	2	9	35.0	42.4-
10	2	9	16.1	15.3-
12	2	9	60.7	64.1-
14	2	9	19.4	19.8
16	2	9	15.4	14.2
-2	2	9	1.0	1.2
-4	2	9	76.0	75.8-
-6	2	9	34.3	38.4
-8	2	9	60.0	57.4
-10	2	9	8.0	10.5-
-12	2	9	8.0	3.7-
-14	2	9	19.7	18.8
-16	2	9	23.9	20.6
-18	2	9	19.2	20.6-
-20	2	9	7.5	3.5
-22	2	9	45.7	56.5-
-24	2	9	19.7	26.8-
-26	2	9	51.6	53.1
	2	10	19.7	29.4-
4	2	10	16.1	26.2-
18	2	10	25.8	29.7
-12	2	10	23.9	33.8
-16	2	10	15.3	18.3
	2	11	15.9	16.9-
2	2	11	48.8	47.4-
20	2	11	41.0	34.9-
-6	2	11	59.7	61.8
-14	2	11	45.5	44.9-
-16	2	11	14.1	22.3
-18	2	11	21.0	28.5
-22	2	11	12.4	12.2
	2	12	7.4	7.4-
8	2	12	22.8	34.8
	2	13	18.5	27.4-
2	2	13	26.6	32.4
10	2	13	49.3	47.7-
14	2	13	36.3	38.9
-8	2	13	15.5	18.0-
-2	2	14	15.7	23.3
1	3		19.5	24.6-
3	3		34.0	43.7-
5	3		38.2	40.4
7	3		11.5	6.4
9	3		85.4	86.5-
11	3		23.0	19.5-
13	3		52.2	44.1
15	3		14.2	13.3
17	3		98.2	101.9
19	3		7.9	1.9
21	3		58.7	50.6-
23	3		19.7	19.1
29	3		12.9	11.2
1	3	1	55.7	94.5
3	3	1	8.5	14.2
5	3	1	86.5	87.2
7	3	1	42.5	32.9-
9	3	1	50.7	50.6-
11	3	1	56.3	59.7
13	3	1	6.7	12.4
15	3	1	57.1	49.0
17	3	1	49.5	32.1
19	3	1	72.9	78.6-
21	3	1	36.6	29.0-
23	3	1	16.0	11.5-
25	3	1	18.9	17.1-
-1	3	1	9.1	15.4
-3	3	1	37.9	42.2
-5	3	1	4.1	.7
-7	3	1	99.4	113.3-
-9	3	1	5.4	3.0-
-11	3	1	61.8	71.8-
-13	3	1	6.6	5.5-
-15	3	1	14.2	6.8-
-17	3	1	7.5	11.2-
-19	3	1	19.3	14.0
-21	3	1	26.4	23.1-
-23	3	1	8.0	2.6
-25	3	1	15.6	11.0-
-29	3	1	31.5	26.8
-31	3	1	17.7	10.3
1	3	2	38.2	37.3-
3	3	2	47.8	47.6
5	3	2	4.7	.7-
7	3	2	143.7	136.6
9	3	2	5.8	3.6
11	3	2	65.4	53.4-
13	3	2	31.4	26.1
15	3	2	28.2	27.9
17	3	2	7.7	1.2-
19	3	2	8.0	10.4
21	3	2	8.1	2.8-
23	3	2	30.5	29.9-
25	3	2	22.4	27.6
27	3	2	7.0	8.4
29	3	2	34.4	32.6-
-1	3	2	110.6	137.5-
-3	3	2	18.8	19.0
-5	3	2	29.7	18.8
-7	3	2	15.1	14.6-
-9	3	2	5.6	8.0-
-11	3	2	34.8	24.9-
-13	3	2	43.7	38.2-
-15	3	2	17.7	22.2
-17	3	2	7.6	7.7
-19	3	2	19.4	30.7-
-21	3	2	16.2	.9
-23	3	2	30.8	31.5
-25	3	2	7.7	12.9
-27	3	2	25.7	36.6
-29	3	2	6.4	5.0
-31	3	2	42.4	31.9-
1	3	3	48.4	47.6
3	3	3	20.6	22.6
5	3	3	44.9	42.8
7	3	3	26.4	20.2
9	3	3	6.2	7.8-
11	3	3	5.7	6.3
13	3	3	56.9	59.3-
15	3	3	18.5	19.2-
17	3	3	80.8	81.0-
19	3	3	19.7	18.0-
21	3	3	52.4	55.9
23	3	3	15.7	17.2-
25	3	3	14.3	12.6
27	3	3	16.5	13.8-
-1	3	3	21.7	11.7-
-3	3	3	12.0	9.0-
-5	3	3	47.6	56.4
-7	3	3	5.6	13.4
-9	3	3	62.0	60.6
-11	3	3	15.9	18.9
-13	3	3	13.9	23.4-
-15	3	3	7.4	6.9-
-17	3	3	71.1	81.2-
-19	3	3	3.0	8.6-
-21	3	3	25.0	23.5-
-23	3	3	8.0	7.3-
-25	3	3	7.6	7.6
-27	3	3	7.1	5.8-
-29	3	3	35.2	23.9
-31	3	3	28.8	19.3-
1	3	4	31.4	21.4-
3	3	4	22.1	20.9
5	3	4	47.9	46.0
7	3	4	6.3	5.5-
9	3	4	6.7	10.5
11	3	4	7.1	2.5-
13	3	4	23.7	21.2-
15	3	4	51.6	45.9
17	3	4	25.4	22.1
19	3	4	58.6	49.1-
21	3	4	25.3	24.0-
23	3	4	18.8	23.9-
25	3	4	17.5	16.0-
27	3	4	35.6	29.0
-1	3	4	5.5	1.0
-3	3	4	100.3	106.3
-5	3	4	11.7	2.4
-7	3	4	20.1	15.2-
-9	3	4	24.9	23.8-
-11	3	4	111.6	113.0-
-13	3	4	27.5	22.3
-15	3	4	49.4	25.6
-17	3	4	7.9	12.1-
-19	3	4	8.0	.6
-21	3	4	16.1	20.9-
-23	3	4	15.8	21.1-
1	3	5	12.7	13.0
3	3	5	51.3	51.7-
5	3	5	6.6	7.6-
7	3	5	63.7	75.4-
9	3	5	7.2	15.7-
11	3	5	25.3	16.7-
13	3	5	7.8	14.1-
15	3	5	30.6	28.8
17	3	5	26.4	22.0-
19	3	5	16.1	12.6
21	3	5	19.1	15.5-
23	3	5	18.0	13.2-
25	3	5	36.4	25.0
27	3	5	14.2	12.4
29	3	5	20.4	22.4
-1	3	5	20.6	11.4-
-3	3	5	50.4	46.1
-5	3	5	101.2	105.4
-7	3	5	30.6	20.8-
-9	3	5	14.0	14.5
-11	3	5	14.6	9.7-
-13	3	5	31.0	16.2-
-15	3	5	62.1	61.4
-17	3	5	8.0	20.7
-19	3	5	8.1	2.0
-21	3	5	6.0	.3-
-23	3	5	15.5	29.3-
-25	3	5	7.2	8.8-
-27	3	5	50.4	37.1-
1	3	6	17.1	12.3-
3	3	6	46.0	30.2-
5	3	6	81.3	79.7
7	3	6	48.3	46.6
9	3	6	60.7	60.1-
11	3	6	7.8	12.1-
13	3	6	57.9	53.6-
15	3	6	23.3	27.6-
17	3	6	45.1	38.1
-1	3	6	6.9	17.3
-3	3	6	22.8	19.0-
-5	3	6	56.2	58.3
-7	3	6	33.0	36.1
-9	3	6	33.9	35.3-
-11	3	6	7.6	4.8
-13	3	6	51.0	44.6
-15	3	6	8.0	5.2-
-17	3	6	26.4	17.1-
-19	3	6	8.0	13.4-
-21	3	6	50.9	64.9-
-23	3	6	14.9	12.6
-25	3	6	36.1	21.8
1	3	7	15.1	15.1-
3	3	7	7.6	2.5-
5	3	7	43.3	34.1
7	3	7	35.7	37.7-
9	3	7	15.9	21.3-
11	3	7	16.1	13.1-
13	3	7	11.4	2.5-
15	3	7	16.0	14.3
17	3	7	7.8	7.6
19	3	7	18.4	30.8
21	3	7	17.1	19.4
-1	3	7	7.5	5.0-
-3	3	7	117.0	135.8-
-5	3	7	7.6	6.2
-7	3	7	50.0	37.7
-9	3	7	7.8	9.0
-11	3	7	51.6	41.9
-13	3	7	11.4	.8
-15	3	7	31.0	27.6
-23	3	7	10.0	12.1-
-25	3	7	20.9	22.0
2	3	8	7.9	14.2-
3	3	8	36.3	42.0-
5	3	8	16.0	20.3-
7	3	8	23.8	16.8
9	3	8	11.4	9.4-
11	3	8	30.9	29.1-
13	3	8	7.9	1.2-
15	3	8	15.5	16.3
17	3	8	7.4	6.6-
19	3	8	17.0	17.0
21	3	8	12.6	16.1-
23	3	8	13.2	16.6-
-1	3	8	51.4	46.4-
-3	3	8	51.4	53.0
-5	3	8	33.2	67.8
-7	3	8	30.7	22.3-
-9	3	8	8.0	2.5
-11	3	8	8.1	5.8-
-13	3	8	26.4	12.7-
-15	3	8	58.1	41.7
-17	3	8	19.2	21.0
1	3	9	36.8	32.7-
3	3	9	19.8	15.4-
5	3	9	8.0	8.9-
7	3	9	11.3	16.8-
9	3	9	36.2	50.0
11	3	9	19.2	22.5
13	3	9	15.1	20.4
21	3	9	31.0	28.3-
23	3	9	31.3	6.4
-1	3	9	16.2	16.7
-3	3	9	11.4	4.4-
-13	3	9	35.8	34.2-
-21	3	9	35.0	34.7
1	3	10	36.1	33.9-
3	3	10	7.9	4.0
5	3	10	19.1	13.9
7	3	10	7.6	7.7-
9	3	10	15.0	13.2
11	3	10	17.7	24.0-
13	3	10	22.5	22.9-
15	3	10	35.9	29.5
17	3	10	23.6	18.2
-1	3	10	7.9	8.9-
-7	3	10	15.7	25.0-
-13	3	10	14.8	23.8
-15	3	10	52.7	46.1
3	3	11	26.1	37.0
5	3	11	10.1	15.4
7	3	11	9.9	12.4
9	3	11	13.4	11.4
11	3	11	31.9	27.7-
-7	3	11	14.6	12.0-
-9	3	11	17.5	20.4-
1	3	12	21.3	25.4-
3	3	12	20.9	28.9-
5	3	12	20.2	23.2
-1	3	12	16.1	13.2
-3	3	12	6.5	3.6-
-5	3	12	16.0	8.7
-7	3	12	12.8	6.1
-9	3	12	40.0	35.4-

The observed and calculated structure factors are shown in Table 7. The IBM 650 and 7070 programs of Shiono (1957, 1959, 1960*a*, 1960*b*, 1961) were used for the computations.

The molecular and the crystal structure

The bond distances and bond angles are shown in Table 8 and Fig. 3. Since the thermal motion of the molecules was not determined the rotational correction (Cruickshank, 1956) for the bond length could not be applied; these corrections will not exceed +0·007 Å in the bond lengths. All the carbon atoms are in a plane within the experimental error. The deviation of the Cl and O atoms from this plane is also very small, and the non-existence of large distortions due to over-crowding in polychlorobenzene derivatives is again supported (Gafner & Herbstein, 1958, 1960; Dean, Richardson & Sakurai, 1961). The deviations from the plane of the benzene ring are shown in Table 9.



(*a*)

(*b*)

Fig. 3. The molecular dimensions. (*a*) Bond distances and (*b*) bond angles.

Table 8. *Bond distances and valency angles*

C_1-C_2	1·373 Å	$C_1-C_2-C_3$	121·6°
C_2-C_3	1·368	$C_2-C_3-C_4$	119·4
C_3-C_4	1·365	$C_3-C_4-C_5$	121·7
C_4-C_5	1·365	$C_4-C_5-C_6$	118·4
C_5-C_6	1·438	$C_5-C_6-C_1$	119·2
C_6-C_1	1·371	$C_6-C_1-C_2$	119·7
C_2-Cl_1	1·704	$C_1-C_2-Cl_1$	118·1
C_3-Cl_2	1·707	$C_3-C_2-Cl_1$	120·3
C_4-Cl_3	1·734	$C_2-C_3-Cl_2$	121·1
C_5-Cl_4	1·673	$C_4-C_3-Cl_2$	119·5
C_6-Cl_5	1·683	$C_3-C_4-Cl_3$	120·3
C_1-O	1·329	$C_5-C_4-Cl_3$	117·9
		$C_4-C_5-Cl_4$	122·6
		$C_6-C_5-Cl_4$	118·9
		$C_5-C_6-Cl_5$	120·3
		$C_1-C_6-Cl_5$	120·5
		C_6-C_1-O	120·4
		C_2-C_1-O	119·8

Standard deviations

C–C	0·018 Å	C–C–C angle	1·2°
C–Cl	0·014	C–C–Cl	1·0
C–O	0·017	C–C–O	1·2

Table 9. *Deviation of the atoms from the plane of the benzene ring*

C_1	−0·003 Å	Cl_1	−0·043 Å
C_2	−0·002	Cl_2	−0·037
C_3	0·001	Cl_3	0·056
C_4	0·004	Cl_4	0·022
C_5	−0·008	Cl_5	0·004
C_6	0·008	O	−0·020

Within the benzene ring, the C_5–C_6 distance is significantly longer than other bond lengths. This might be due to an effect of intermolecular hydrogen bonding which is discussed later. The C–O distance of 1·33 Å is the same order of the magnitude for the similar compounds, e.g. tetrachlorohydroquinone (Sakurai, 1962), resorcinal (Robertson, 1936; Bacon & Carry, 1956), hydroquinone clathrate (Palin & Powell, 1947).

The arrangement of the molecule in the crystal is shown in Fig. 4. The molecular plane makes an angle of 45·1° with *ac* plane. The direction cosines of the molecular axis with respect to the orthogonal crystal axes *a'*, *b* and *c* are shown in Table 10.

Comparison of the n.q.r. and X-ray results are shown in Tables 2 and 3. With the exception of the angle between the Cl_4 and $Cl_5\sigma$ bonds, the agreement is good.

Intermolecular distances shorter than 4·0 Å are listed in Table 11 and shown in Fig. 4. The distances

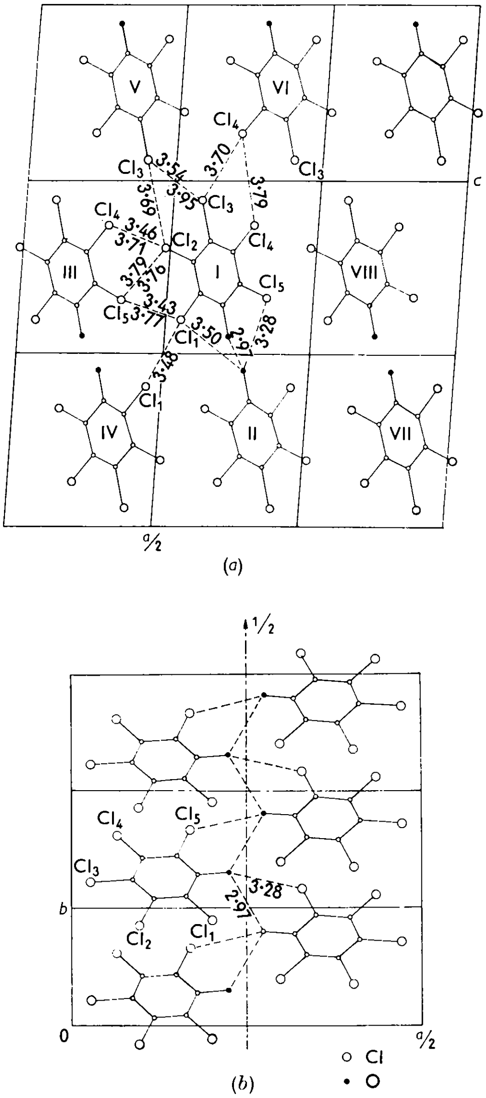


Fig. 4. The molecular arrangement in the crystal. (a) Projection on (010). (b) Projection on (001).

Table 10. *Direction cosines of molecular axes*

	a'	b	c
L	0·177	−0·704	−0·688
M	−0·982	−0·075	−0·176
N	0·074	0·706	−0·704

between $Cl_1(I) \cdots Cl_1(IV)$, $Cl_1(I) \cdots Cl_5(III)$ and $Cl_2(I) \cdots Cl_4(III^-)$ are slightly shorter than the ordinary Van der Waals distance of 3·6 Å; similar $Cl \cdots Cl$ distances were found in tetrachlorohydroquinone (Sakurai, 1962) and 2,5-dichloroaniline (Sakurai, Sundaralingam & Jeffrey, 1963).

The hydrogen bonding

The configuration around the hydroxyl group is very similar to that found in the crystal structure of tetrachlorohydroquinone. These are shown in Fig. 5 and Table 12. In Fig. 5, dotted lines represent the unit cell of the tetrachlorohydroquinone.

Table 11. *Intermolecular atomic distances*

Roman figures in the parentheses correspond to the molecule in Fig. 4, and their coordinates are deduced from those in Table 6 by following relations

$Cl_1(I) \cdots Cl_1(IV)$	3·48 Å	$Cl_3(I) \cdots Cl_4(VI)$	3·70 Å
$Cl_1(I) \cdots Cl_5(III)$	3·43	$Cl_3(I) \cdots Cl_3(V)$	3·95
$Cl_1(I) \cdots Cl_5(III^-)$	3·77	$Cl_3(I) \cdots Cl_3(V^-)$	3·54
$Cl_1(I) \cdots Cl_5(I^-)$	3·88	$Cl_3(I) \cdots Cl_4(I^-)$	3·80
$Cl_2(I) \cdots Cl_3(I^-)$	3·96	$Cl_4(I) \cdots Cl_4(VI)$	3·79
$Cl_2(I) \cdots Cl_3(V^-)$	3·69	$Cl_1(I) \cdots O(I^-)$	3·64
$Cl_2(I) \cdots Cl_4(III)$	3·71	$Cl_1(I) \cdots O(II^-)$	3·50
$Cl_2(I) \cdots Cl_4(III^-)$	3·46	$Cl_5(I) \cdots O(I^+)$	3·84
$Cl_2(I) \cdots Cl_4(I^-)$	3·88	$Cl_5(I) \cdots O(II)$	3·28
$Cl_2(I) \cdots Cl_5(III)$	3·76	$O(I) \cdots O(II)$	2·97
$Cl_2(I) \cdots Cl_5(III^-)$	3·79		

(I) x, y, z (I^+) $x, 1+y, z$ (I^-) $x, -1+y, z$
(II) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$, ($II^-$) $\frac{1}{2}-x, -\frac{1}{2}+y, \frac{1}{2}-z$
(III) $x, 1-y, -\frac{1}{2}+z$ (III^-) $x, -y, -\frac{1}{2}+z$
(IV) $\frac{1}{2}-x, -\frac{1}{2}+y, -z$ (V) $-x, 1-y, -z$ (V^-) $-x, -y, -z$
(VI) $-x, y, \frac{1}{2}-z$

Table 12. *Distance and angles around hydroxyl group*

	Penta chloro phenol	Corresponding values in tetrachloro-hydroquinone
$O \cdots O$ distance	2·97 Å	2·92 Å
$O \cdots Cl_5$	3·28	3·29
C_1–O	1·33	1·35
$C_1(I) \cdots O(I) \cdots O(II)$ angle	125·0	126·8
$C_1(I) \cdots O(I) \cdots O(II^-)$	120·2	117·1
$O(II) \cdots O(I) \cdots O(II^-)$	112·1	111·8

Since $O \cdots O$ bond length corresponds to an unusually long hydrogen bond and the $O \cdots Cl_5$ is shorter than the normal Van der Waals approach, a bifurcated hydrogen bond between $\text{O–H}\begin{smallmatrix} \diagup O \\ \diagdown Cl \end{smallmatrix}$ was suggested in the tetrachlorohydroquinone. The posi-

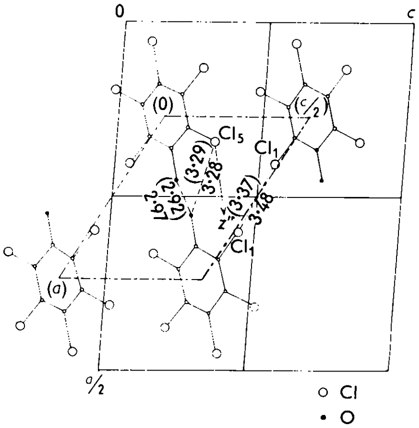


Fig. 5. Comparison with tetrachlorohydroquinone. —·—·— Cell for tetrachlorohydroquinone. Figures in parentheses correspond to tetrachlorohydroquinone. Z'' is an principal axis of the intermolecular field gradient.

tion of the hydrogen was also indicated from a peak in the three-dimensional difference Fourier synthesis in the tetrachlorohydroquinone. However in the presence of the chlorine atoms, the residual peak in the difference synthesis might not necessarily correspond to the hydrogen position (Sakurai, Sundaralingam & Jeffrey, 1963). The present molecule is even more unfavorable for hydrogen atom location because of the five chlorine atoms, and the difference synthesis was not attempted. However, the n.q.r. results clearly showed the effect of the proton on the Cl_5. The Cl_5 resonance differs from that of the other chlorine nuclei in four respects:

(1) the intensity of the pure quadrupole resonance is weaker (Table 1);
(2) the asymmetry parameter is smaller (Table 1);
(3) the frequency separation from Cl_1 (0·31 m.c.) is larger than that between Cl_2 and Cl_4; and it is greater than normally associated with intermolecular interactions (Table 1);
(4) the C–Cl_5 bond direction shows the only significant disagreement with the X-ray data (Table 2 and Table 13).

Although the intensity of the resonance frequency was not obtained quantitatively by the super regenerative oscillator, reliable qualitative results were obtained. The Cl_3 resonance is strong, Cl_1, Cl_2, Cl_4 are medium and Cl_5 is weak. Since the C–Cl_3 bond is almost perpendicular to the high frequency magnetic field and the other C–Cl bonds make about 50° to the field, the Cl_3 resonance is naturally stronger than the others. The weakness of the Cl_5 resonance can be attributed to the magnetic interaction of the proton. The surrounding magnetic nuclei affect the resonating nucleus through dipole interaction and indirect spin–spin interaction. Since the hydrogen bond is believed to be mainly electrostatic in character rather than due to the sharing of bond electrons, the spin–spin interaction can be assumed to be negligible. The dipole-dipole interaction energy is given by

$$\Delta\nu = (\mu/r^3)2\cdot 1 \times 10^{-21}$$

in frequency units for the chlorine nucleus, where μ is the magnetic moment of the surrounding nucleus in nuclear magneton units and r is the internuclear distance (Das & Hahn, 1958). Both the chlorine and the proton contribute with μ's of 0·82 and 2·79 respectively. The nearest chlorine–chlorine distance is about 3·1 Å and the corresponding interaction energy is about 0·06 kcyc., while if proton exists at 2·5 Å from the Cl_5 the interaction energy is 0·4 kcyc. The line width was not measured in the present experiment. However, it is estimated to be of the order of 2 kcyc. for this type of compound if special intermolecular interactions do not exist (Ayant, 1951; Wang, 1955). Therefore the magnetic interaction of the proton estimated above will considerably increase the line width and reduce the apparent peak height of Cl_5. If the line shape could be accurately measured by means of a regenerative spectrometer on both deuterated and undeuterated sample, this will provide data from which the chlorine proton distance could be calculated.

The 2nd, 3rd and 4th effects can also be attributed to the electrostatic interactions. A similar effect was observed in tetrachlorohydroquinone.

The observed electric field gradient is the superposition of the intramolecular effect and the intermolecular effect. An attempt was made to estimate the intermolecular effect at the Cl_5 nucleus from an evaluation of the intramolecular field gradient. In order to determine the direction of the observed field gradient accurately with respect to the crystallographic axes, a' and c were redetermined so that the direction cosines of all σ bonds obtained by n.q.r. agreed with X-ray result, as clearly as possible. The discrepancy between n.q.r. and X-ray σ bonds was then less than one degree for Cl_1 through Cl_4 but 2·3 degrees for Cl_5. The direction cosines of the observed field gradient were obtained from the principal axes of the ellipse of zero splitting loci. The field gradient along each axis was obtained from the frequency and the asymmetry parameter using the relations

$$h\nu = \frac{eQV_{zz}}{2}\left(1+\frac{\eta^2}{3}\right)^{\frac{1}{2}}, \qquad \eta = \frac{V_{xx}-V_{yy}}{V_{zz}}$$

where, V_{xx}, V_{yy} and V_{zz} are field gradients along the principal axes e is the electron charge and Q is the nuclear quadrupole moment, which is $0\cdot 0789 \times 10^{-24}$ cm.^{2} for Cl^{35}.

The principal axes of the intramolecular field gradient were assumed to be along the C–Cl_5 bond and the normal of the benzene ring, obtained from the X-ray data. For the field gradient along each axis, the value for Cl_1 was used since this nucleus is symmetrically situated with respect to Cl_5 and the intermolecular effect will be small.

The observed and intramolecular field gradients are shown in Table 13.

Table 13. *The field gradient at the* Cl_5 *nucleus*

(a) Observed field gradient

	The direction cosines of the principal axes			The field gradient along the principal axes		
	a'	b	c			
X	0·172	0·662	−0·730	−12·0	10^{24}	e.cm.$^{-2}$
Y	−0·909	0·392	0·142	−14·7		
Z	0·381	0·641	0·666	−26·7		

(b) Calculated intramolecular field gradient

	The direction cosines of the principal axes			The field gradient along the principal axes		
	a'	b	c			
X'	0·074	0·706	−0·704	−11·2	10^{24}	e.cm.$^{-2}$
Y'	−0·935	0·295	0·198	−15·7		
Z'	0·348	0·648	0·677	26·9		

Table 14. *The intermolecular field gradient*

	The direction cosines of the principal axes			The field gradient along the principal axes		
	a'	b	c			
X''	−0·068	0·732	−0·677	−1·2	10^{24}	e.cm.$^{-2}$
Y''	−0·209	0·658	0·723	−0·8		
Z''	0·978	0·191	0·106	2·0		

The calculated intramolecular field gradient was subtracted from that observed and the residual intermolecular field gradient was transformed into its principal axes. The results are shown in Table 14.

This field gradient has 20% asymmetry, but this is not significant. The main effect is the positive charge along Z'' axis. If this is due to a point charge ϱ, r Å, from the Cl_5 nucleus, the field gradient is expressed by the form

$$-V_{zz}=2(1+|\gamma|)/r^3\varrho\ ,$$

where γ is the Sternheimer factor (Sternheimer, 1951; Sternheimer & Foley, 1956). This factor for neutral chlorine is not known exactly, but will be about 30 (Das & Hahn, 1958). Therefore if the point charge is 2·5 Å from the chlorine, ϱ is about 0·5 in the unit of proton charge, which is reasonable for the hydrogen bond. The Z'' direction, shown in Fig. 5, does not agree well with the supposed direction of the $Cl_5\cdots H$.

While this calculation gives a satisfactory qualitative estimate of the effect of the proton, it is not quantitatively satisfactory for two reasons. The first is that it depends on the small difference of two large quantities and is subjected to the large error. The second is that the intramolecular effect is not the same for Cl_5 and Cl_1 because the shape of the molecule is not strictly symmetrical, as shown in Fig. 3. However, the proton does appear to have a definite interaction with both the adjacent oxygen and chlorine atoms and this configuration may be called bifurcated hydrogen bond between $\mathrm{O{-}H}\begin{smallmatrix}\cdot\cdot\cdot\mathrm{O}\\ \cdot\cdot\cdot\mathrm{Cl}\end{smallmatrix}$.

The pseudo structure in the phase determination

At the initial stage of the two-dimensional structure analysis, a molecular center at $X=0·135$ and $Z=0·187$ was obtained from rough molecular structure factor calculation. The calculated Fourier map corresponding to this structure showed molecular shape and it was refined by repeated Fourier syntheses. However, it was soon noticed that some of the peaks were not circular and the R factor slowly converged to 29%. These coordinates are shown in Table 15 and Fig. 6.

A careful re-examination of the molecular structure factor then gave a second solution for the molecular center at $X=0·135$ and $Z=0·157$, and from this position two cycles of refinement reduced the R factor to 14%. The true molecular center coordinates after refinement are $X=0·132$ and $Z=0·165$. Of the 209 reflections in this projection, the signs of 56 were incorrect in the pseudo structure.

Table 15. *The pseudo solution*

	x	z		x	z
Cl_1	0·2033	0·0640	C_2	0·163	0·130
Cl_2	0·0990	−0·0025	C_3	0·116	0·091
Cl_3	0·0294	0·1109	C_4	0·090	0·150
Cl_4	0·0683	0·3020	C_5	0·102	0·226
Cl_5	0·1722	0·3575	C_6	0·148	0·247
C_1	0·181	0·203	O	0·226	0·239

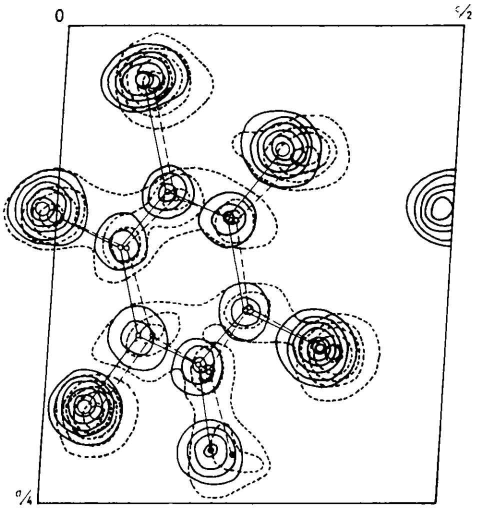


Fig. 6. The relation between the true and the pseudo structure. ——(*a*) True structure. – – –(*b*) Pseudo structure.

The pseudo homometric solution (Luzzati, 1953) is not unusual (Donohue & Trueblood, 1956; Watase, Tomiie & Nitta, 1958). However, in this analysis, all the atoms in the pseudo structure are situated so close to the true atomic positions as to be within about the 4 e.Å^{-2} contours of corresponding atomic peak of true

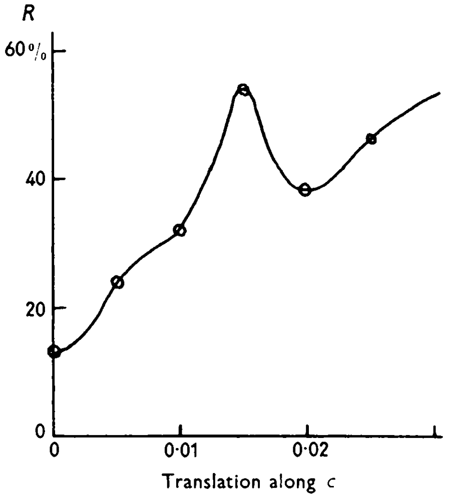


Fig. 7. Change of R factor due to the c translation.

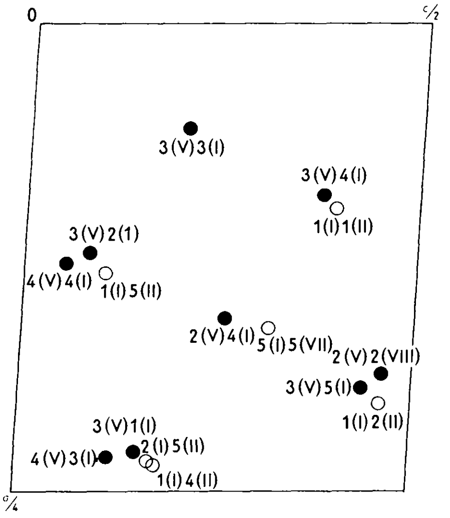


Fig. 8. A part of the two-dimensional Patterson peaks. 1(I) 5(II) means a vector from chlorine 1 of the molecule I to the chlorine 5 of the molecule II, etc.

Fourier map and both Fourier maps overlap each other (Fig. 6). The reason for the appearance of this unusual pseudo solution can be readily shown.

The main difference between these two structures is a translation along c axis. An actual calculation showed that the R factor has subsidiary minimum at 0·02 of c translation (Fig. 7). Starting from this minimum, R factor could be reduced by a slight deformation of the molecule, but could not converge to the true structure over the 'potential barrier' of the R factor. The Patterson function of this structure explains this subsidiary minimum. On this projection, the plane group is $P2$ with $a'=a/2$ and $c'=c/2$. Two molecules exist in the cell $a'c'$. If one molecule is represented by M, the other molecule $\overline{M}$ is related to M by the center of symmetry of this projection. The interatomic vectors which are affected by the translation are those between molecule M and $\overline{M}$. These peaks in an asymmetric unit on this projection are shown in Fig. 8. Only chlorine–chlorine vectors are considered. The vector from M, for instance I in Fig. 4, to $\overline{M}$ are expressed by white circles and those from $\overline{M}$, for instance V in Fig. 4, to M are expressed by black circles. In this figure many black and white circles appear as pairs or groups. In each group, the white circle appears at right hand side of the black circle. If the molecule M moves to the right, $\overline{M}$ to the left. Then the white circles move to left and the black ones to right. At a translation about 0·02, many of the black and white circles are interchanged and the Patterson function looks like the original one. Thus the R factor has its minimum at this position.

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