An X-ray Analysis of the Structure of Hexachlorobenzene, using the Fourier Method.


(Communicated by Sir William Bragg, F.R.S.—Received June 26, 1931.)

Introduction.

A recent analysis of \( \text{C}_6(\text{CH}_2)_6 \)* showed that the benzene nucleus in that compound is similar, both in structure and in dimensions, to the plane ring of six carbon atoms, each of diameter 1·42 A., previously known to exist in graphite.†

That being so, it was clear that other benzene compounds should be examined as carefully as possible, to see whether the benzene nucleus is always of the same shape and size. The fully substituted derivatives seemed most likely to give the information desired.

The present paper is concerned with the structure of one such derivative, C\(_6\)Cl\(_6\), whose crystals are sufficiently large and stable at room temperatures to be examined in detail by the X-ray ionisation spectrometer and other methods.

A few previous measurements are recorded. H. Mark‡ quotes a dissertation by W. Schneefussz (Berlin) giving the dimensions of the unit cell, and the molecular symmetry, for C\(_6\)Cl\(_6\) and also for C\(_6\)Br\(_6\). W. G. Plummer§ found approximately the same dimensions, using the powder method, for both these compounds, and comes to similar conclusions concerning the number and symmetry of the molecules. The results obtained, however, were quite inadequate to provide any indication of the detailed structure of the unit cell.

Experimental Details.

The material for the present investigation was very kindly given to me by Professor C. K. Ingold. Slow recrystallisation gave small needle-shaped crystals, extended along the [010] direction, but with good side faces \(\{100\}\) \(\{001\}\) \(\{10\}\), and end faces \(\{11\}\). As recorded by P. Groth|| the \(\{001\}\) is a good cleavage plane and secondary cleavage occurs also on \(\{100\}\) and \(\{10\}\), while

§ ‘Phil. Mag.,’ vol. 50, p. 1214 (1925).
bent or curved crystals are common, owing to easy slipping along (11\overline{1}) planes. Groth also mentions the occasional occurrence of forms \{307\} and \{702\}. These planes were not visually observed in the present investigation; (307) gave a small second order reflection, but (702) was not found even on the ionisation spectrometer.

The crystal density is 2\cdot044 gr. per cubic centimetre.

The unit cell is simple monoclinic prismatic, with

\[
\begin{align*}
a &= 8\cdot07 \\
b &= 3\cdot84 \\
c &= 16\cdot61 \text{ A.}
\end{align*}
\]

\[\beta = 116^\circ 52',\]

and it contains two molecules of \(\text{C}_6\text{Cl}_4\).

The space-group is most probably \(\text{C}^5_{2h}(\text{P}2_1/\text{c})\). From the \{h0l\} planes 80 reflections were observed and measured on the ionisation spectrometer (Mb anticathode). For all these \(l\) was even. Careful search failed to reveal any reflection from a plane having an odd index \(l\). Also, although (020) gave a small reflection, no reflection could be found from (010), (030) or any other order of the symmetry plane. This plane, however, forms the cross section of the needle-shaped crystals and is in a most unfavourable position for examination on the ionisation spectrometer. Mr. Pelton, of the Davy Faraday Laboratory, very kindly examined the (0k0) planes by the oscillation photographic method, using Cu radiation and a cylindrical camera. He found no trace of any reflection except from the (020) plane, which gave a weak reflection, thus confirming the ionisation spectrometer results.

**Structure Determination by Trial and Error.**

The 12 carbon and 12 chlorine atoms in the unit cell may therefore be divided each into three sets of four, having the co-ordinates:

**C atoms—**

\[
\begin{align*}
x_1 y_1 z_1 &= -x_1 -y_1 -z_1 \\
x_2 y_2 z_2 &= -x_2 -y_2 -z_2 \\
x_3 y_3 z_3 &= -x_3 -y_3 -z_3
\end{align*}
\]

\[
\begin{align*}
x_1 \frac{1}{2} - y_1 \frac{1}{2} + z_1 &= -x_1 \frac{1}{2} + y_1 \frac{1}{2} - z_1 \\
x_2 \frac{1}{2} - y_2 \frac{1}{2} + z_2 &= -x_2 \frac{1}{2} + y_2 \frac{1}{2} - z_2 \\
x_3 \frac{1}{2} - y_3 \frac{1}{2} + z_3 &= -x_3 \frac{1}{2} + y_3 \frac{1}{2} - z_3
\end{align*}
\]

**Cl atoms—**

\[
\begin{align*}
X_1 Y_1 Z_1 &= -X_1 -Y_1 -Z_1 \\
X_2 Y_2 Z_2 &= -X_2 -Y_2 -Z_2 \\
X_3 Y_3 Z_3 &= -X_3 -Y_3 -Z_3
\end{align*}
\]

\[
\begin{align*}
X_1 \frac{1}{2} - Y_1 \frac{1}{2} + Z_1 &= -X_1 \frac{1}{2} + Y_1 \frac{1}{2} - Z_1 \\
X_2 \frac{1}{2} - Y_2 \frac{1}{2} + Z_2 &= -X_2 \frac{1}{2} + Y_2 \frac{1}{2} - Z_2 \\
X_3 \frac{1}{2} - Y_3 \frac{1}{2} + Z_3 &= -X_3 \frac{1}{2} + Y_3 \frac{1}{2} - Z_3
\end{align*}
\]

There are 18 unknown parameters to be determined.
In the case of C$_6$(CH$_3$)$_6$ a definite lead was given in this direction:

(a) By the pseudo-hexagonal structure of the [001] zone, revealed by the observed structure factors in that zone (i.e., intensities of reflection corrected for angle). In particular, the intense reflections from certain small-spacing planes helped to "place" the atoms with considerable certainty.

(b) By the intense reflection from the main cleavage (001) plane, and by the independence of "l" of the observed structure factors for all planes \{hkl\}.

Obviously it is necessary to seek some similar indications, if possible, in the case of C$_6$Cl$_6$. The needle-shaped crystals are themselves pseudo-hexagonal in form, since

\[ d_{100} = 7.20 \quad d_{10\bar{2}} = 6.98 \quad d_{002} = 7.41 \text{ Å.} \]

and

\[ 100 : 10\bar{2} = 56° 59' \quad 10\bar{2} : 001 = 59° 53' \quad 001 : 100 = 63° 8'. \]

The relative intensities of reflection from all possible \{h0l\} planes were carefully measured and divided into three groups:—

1. Those lying in the acute angle between (001) and (100).
2. Those lying in the acute angle between (100) and (10\bar{2}).
3. Those lying in the acute angle between (10\bar{2}) and (001).

These are plotted in fig. 1.

The high absorbing power of Cl for Mb radiation has a noticeable influence on the resulting graphs. The crystal used (that giving the best reflections) was of the cross section shown in fig. 2 (a), the distance AB being 1.3 mm., whereas CD was about 0.6 mm. The absorption therefore, was least in the region of the (001) plane, the crystal as a whole being bathed in the X-ray beam, and greatest in the region of (10\bar{1}). A smaller, but much more evenly developed crystal (fig. 2 (b)) in which approximately AB = CD = EF = 0.75 mm., gave reflections of very nearly equal intensity from the planes (10\bar{6}), (30\bar{4}) and (202), these reflections being the largest actually observed. Using this fact, it was not difficult to make an approximate correction for absorption in the larger crystal. This was done, and the usual corrections were also applied to the observed intensities to obtain "experimental" values of the structure factors for the different planes.

These are shown in fig. 3. Here allowance has also been made for the falling off of atomic scattering power with angle, using an F curve for chlorine based on that given by James and Firth,* but modified to take account of the

Fig. 1.—Observed Intensities.
probability that the atoms are not ionised; and an $F$ curve for carbon similar to that adopted in the $C_6(CH_3)_6$ investigation (loc. cit.). This correction need only

![Diagram](image)

**Fig. 2 (a) and (b).**

be approximate, since it has only to be used in the preliminary determination of the structure factor signs.

Fig. 3 shows that in $C_6Cl_6$, as in $C_6(CH_3)_6$, one zone has a distinctly hexagonal structure. The correspondence between the three sets of structure factors is well marked. This considerably simplifies the problem of determining the unknown parameters, since if $x_1, z_1, X_1, Z_1$ can be found, the corresponding parameters for the remaining five carbon and five chlorine atoms are known at any rate approximately. A further simplification follows from the fact that the scattering power of chlorine is nearly three times as great as that of carbon, so that the exact location of the carbon atoms is not essential for a first estimate of the structure factors.

The problem of finding $X_1$ and $Z_1$ (and hence the positions of all chlorine atoms in the [010] projection) was tackled as follows. Attention was first concentrated on the various even orders of reflection from the (001) plane, to see if agreement could be obtained between observed and calculated structure factors for these 10 orders. This would give $Z_1, Z_2$ and $Z_3$. Since the carbon atoms are relatively unimportant, it was merely assumed, as a first approximation, that these are distant 1.42 A. from the origin, along lines making angles

$$\pm \theta, \quad \pm \left(\frac{\pi}{3} + \theta\right), \quad \pm \left(\frac{2\pi}{3} + \theta\right)$$
with the $a$ axis. Then if the chlorine atoms are distant $R$ from the origin along the same directions,

$$X_1 = \frac{R \sin (\beta - \theta)}{\sin \beta}, \quad Z_1 = \frac{R \sin \theta}{\sin \beta},$$

Thus $R$, $\theta$ have become the two independent variables in place of $X$, $Z$. 
The calculated structure factor for any even order (001), assuming both Cl and C atoms to be not ionised, is given by

\[ S \propto \left[ 6 \left( \cos 2\pi \left( \frac{l \cdot 1.42}{c \sin \beta} \cdot \sin \theta \right) + \cos 2\pi \left( \frac{l \cdot 1.42}{c \sin \beta} \cdot \sin \left( \frac{\pi}{3} + \theta \right) \right) \right] 
+ \cos 2\pi \left( \frac{l \cdot 1.42}{c \sin \beta} \cdot \sin \left( \frac{2\pi}{3} + \theta \right) \right) \right] 
+ 17 \left[ \cos 2\pi \left( \frac{l \cdot R}{c \sin \beta} \cdot \sin \theta \right) + \cos 2\pi \left( \frac{l \cdot R}{c \sin \beta} \cdot \sin \left( \frac{3\pi}{3} + \theta \right) \right) \right] 
+ \cos 2\pi \left( \frac{l \cdot R}{c \sin \beta} \cdot \sin \left( \frac{2\pi}{3} + \theta \right) \right) \right].

θ was varied from 0° to 30° by 5° at a time, and R varied from (2 × 1.42) Å, to (2.7 × 1.42) Å by (0.05 × 1.42) Å, at a time, the latter range being taken as likely to cover all possible values of the chlorine atom radius. Subsequently the range was limited still further until finally it was found that the values θ = 19° and R = 2.18 × 1.42 = 3.10 Å gave the best agreement for all the 10 orders in question.

\[
\begin{array}{cccccccccc}
(002) & (004) & (006) & (008) & (0010) & (0012) & (0014) & (0016) & (0018) & (0020) \\
\text{Obs. . . . .} & 37 & 49 & 54 & 100 & <23 & 96 & 164 & <56 & 110 <110 \\
\text{Calc. . . .} & 33 & 59 & 64 & 100 & 19 & 102 & 203 & 63 & 125 11
\end{array}
\]

The higher orders were particularly sensitive to small changes either in θ or in R. It is fairly certain therefore that the value of Z is fixed to within a few per cent. for the chlorine atoms. The above test does not, of course, decide the value of X, but this is fixed by a corresponding comparison for the various orders of reflection from the (100) plane. The close correspondence between the observed structure factors for (002) . . . (0020) and for (100) . . . (1000) implies that 2Z/c and X/a cannot greatly differ. The above values of R, θ give for 2Z/c, etc., the values ±49.0°, ±98.7°, ±147.5°, when expressed in angular measure. The best agreement for (100) . . . (1000) is obtained for X/a = ±46.2°, ±100.2°, ±146.5°.

\[
\begin{array}{cccccccccc}
(100) & (200) & (300) & (400) & (500) & (600) & (700) & (800) & (900) & (1000) \\
\text{Obs. . . . .} & 35 & 41 & 37 & 100 & <32 & 83 & 132 & <79 <110 <156 \\
\text{Calc. . . .} & 31 & 47 & 40 & 100 & 34 & 96 & 173 & 62 & 97 65
\end{array}
\]

A similar test was carried out for 10 orders of reflection from (102), and
agreement was found to be best when the angular distances of the Cl atoms from the plane (10\(\overline{2}\)) were also \(\pm 46.2^\circ\), \(\pm 100.2^\circ\), and \(\pm 146.5^\circ\).

\[
(10\overline{2}) \quad (20\overline{4}) \quad (30\overline{5}) \quad (40\overline{8}) \quad (50\overline{10}) \quad (60\overline{12}) \quad (70\overline{14}) \quad (80\overline{16}) \quad (90\overline{18}) \quad (100\overline{20})
\]

<p>| | | | | | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Obs.</td>
<td>38</td>
<td>36</td>
<td>32</td>
<td>100</td>
<td>&lt;32</td>
<td>99</td>
<td>154</td>
</tr>
<tr>
<td>Calc.</td>
<td>31</td>
<td>47</td>
<td>40</td>
<td>100</td>
<td>34</td>
<td>96</td>
<td>173</td>
</tr>
</tbody>
</table>

These conclusions are shown graphically in fig. 4.

![Graphical representation of X-ray analysis](image)

**Fig. 4.**

It is clear that the chlorine atoms have been satisfactorily located, since the three sets of parameters very nearly intersect.

Taking as mean values

\[
X_1 = 3.225 \quad X_2 = 2.26 \quad X_3 = 1.14
\]

and

\[
Z_1 = 1.155 \quad Z_2 = 3.46 \quad Z_3 = -2.26
\]

fig. 5 gives the resulting structure factors for all the planes (002) .. (102) .. (100), still assuming as before that the carbon atoms are distant \(1.42\) A. from the origin along the lines joining the origin to the chlorine atoms, i.e., that

\[
x_1 = 1.435 \quad x_2 = 1.01 \quad x_3 = 0.515
\]

and

\[
z_1 = 0.51 \quad z_2 = 1.525 \quad z_3 = -1.015.
\]
The correspondence between figs. 3 and 5 shows that we are justified in adopting these parameters as a means of determining the signs of the experimentally found structure factors. A knowledge of these signs is, of course, necessary before a Fourier analysis of the results can be carried out.*

Table II.

| 13 | 16  | 28  | 34  | 34  | 42  | 31  | 12  | 18  | 29  | 21  | 20  | 33  | 32  | 25  | 32  | 33  | 20  | 21  | 29  | 18  | 12  | 31  | 42  | 34  | 34  | 38  | 28  | 16  | 13  |
|----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| 22 | 20  | 23  | 31  | 35  | 29  | 31  | 40  | 29  | 10  | 14  | 30  | 32  | 30  | 28  | 19  | 29  | 38  | 27  | 28  | 63  | 79  | 45  | 18  | 27  | 34  | 28  | 33  | 40  | 31  | 22  |
| 33 | 29  | 32  | 35  | 37  | 33  | 23  | 25  | 37  | 33  | 22  | 30  | 44  | 42  | 34  | 29  | 28  | 32  | 30  | 41  | 90  | 146 | 128 | 35  | 22  | 26  | 29  | 23  | 31  | 39  | 33  |
| 35 | 26  | 24  | 28  | 34  | 38  | 36  | 26  | 28  | 40  | 36  | 25  | 28  | 36  | 37  | 35  | 38  | 36  | 29  | 34  | 76  | 143 | 167 | 112 | 42  | 46  | 36  | 27  | 20  | 32  | 35  |
| 35 | 35  | 30  | 18  | 12  | 16  | 33  | 39  | 31  | 27  | 31  | 26  | 18  | 17  | 23  | 25  | 31  | 36  | 35  | 29  | 39  | 76  | 110 | 103 | 63  | 39  | 38  | 31  | 18  | 23  | 35  |
| 32 | 50  | 68  | 69  | 42  | 8  | 5  | 27  | 38  | 29  | 23  | 28  | 29  | 23  | 20  | 22  | 23  | 27  | 32  | 32  | 27  | 29  | 41  | 47  | 42  | 40  | 43  | 37  | 34  | 21  | 32  |
| 29 | 41  | 89  | 136 | 136 | 72  | 12  | 5  | 25  | 33  | 30  | 33  | 41  | 40  | 31  | 28  | 34  | 34  | 29  | 30  | 31  | 29  | 29  | 31  | 27  | 29  | 29  | 42  | 48  | 40  | 32  | 29  |
| 31 | 25  | 47  | 112 | 168 | 137 | 58  | 12  | 15  | 23  | 29  | 34  | 40  | 38  | 30  | 24  | 27  | 37  | 38  | 28  | 29  | 34  | 38  | 44  | 46  | 38  | 35  | 45  | 48  | 40  | 31  |
| 29  | 26  | 25  | 49  | 99  | 114 | 71  | 28  | 24  | 27  | 16  | 22  | 33  | 25  | 17  | 22  | 28  | 28  | 29  | 28  | 28  | 35  | 38  | 38  | 50  | 61  | 52  | 42  | 41  | 37  | 29  |
| 38  | 37  | 40  | 36  | 37  | 49  | 46  | 29  | 31  | 37  | 24  | 19  | 32  | 29  | 10  | 28  | 70  | 73  | 45  | 27  | 28  | 36  | 40  | 33  | 35  | 61  | 78  | 62  | 43  | 39  | 38  |
| 58  | 63  | 58  | 51  | 36  | 26  | 28  | 32  | 33  | 37  | 33  | 26  | 38  | 44  | 17  | 18  | 89  | 147 | 119 | 57  | 31  | 34  | 38  | 36  | 33  | 47  | 77  | 80  | 54  | 44  | 57  |
| 56  | 81  | 74  | 53  | 44  | 35  | 27  | 31  | 36  | 34  | 30  | 26  | 33  | 45  | 30  | 7  | 49  | 140 | 166 | 103 | 43  | 33  | 38  | 47  | 40  | 60  | 51  | 63  | 51  | 37  | 56  |
| 36  | 64  | 77  | 57  | 42  | 45  | 39  | 24  | 24  | 31  | 33  | 28  | 26  | 31  | 33  | 17  | 17  | 70  | 124 | 107 | 50  | 31  | 47  | 57  | 58  | 50  | 36  | 31  | 33  | 30  | 36  |
| 29  | 37  | 55  | 56  | 41  | 43  | 55  | 36  | 17  | 30  | 37  | 39  | 29  | 23  | 27  | 29  | 24  | 31  | 59  | 71  | 47  | 47  | 26  | 40  | 66  | 79  | 74  | 47  | 17  | 14  | 25  | 29  |
| 25  | 22  | 31  | 47  | 46  | 36  | 42  | 45  | 33  | 24  | 32  | 38  | 32  | 23  | 22  | 27  | 29  | 27  | 30  | 39  | 40  | 31  | 29  | 43  | 66  | 79  | 63  | 27  | 7  | 16  | 25  |
| 20  | 14  | 15  | 39  | 58  | 52  | 36  | 33  | 36  | 35  | 33  | 31  | 28  | 25  | 24  | 24  | 24  | 25  | 28  | 31  | 33  | 35  | 36  | 33  | 36  | 52  | 58  | 39  | 15  | 14  | 20  |

K \{ S(x, z) + \text{arbitrary constant.} \}

X-Ray Analysis of Structure of Hexachlorobenzene.

545
These factors are, of course, not now corrected for falling off of atomic scattering power with angle. No "temperature factor" has been added, which may account for the fact that the higher terms, which will terminate the Fourier series, are still relatively large.

A complication is introduced into the summation of the Fourier series

\[ S(x, z) = \sum \sum F(h0l) \cos 2\pi (hx/a + lz/c), \]

because the experimental structure factors given in Table I are not absolute, but only relative. In other words \( F(000) \), the first and constant term of the series, is not known. This will necessarily limit the amount of information that can be obtained from the resulting contour diagram. It will not, however, affect either the positions of the atomic centres, or the shapes of the contours. If the Fourier series were complete, \( S(x, z) \) would be positive everywhere.

![Fig. 6.—Projection on (010) Plane.](image-url)
F(000) was therefore arbitrarily given such a value as to bring this about, and Table II shows the values of S(x, z) so obtained.

It must be remembered, however, that these values are measured in arbitrary units and are subject to the addition of an unknown constant. Any attempt at electron counting, for example, is out of the question.

The contour diagrams shown in figs. 6 and 7 are drawn for values of S(x, z) of 20, 50, 80, 110, 140, 170; also (in fig. 7) for 30 and 40 within the benzene ring.

![Diagram](image)

**Fig. 7.**—Projection of C₆Cl₆ Molecule.

Certain features are at once apparent.

(1) The molecule is quite clearly defined, the positions of the atoms being not far from those used in the preliminary sign determination.

<table>
<thead>
<tr>
<th>Trial and error parameters.</th>
<th>Fourier analysis parameters.</th>
</tr>
</thead>
<tbody>
<tr>
<td>X₁ 3·225</td>
<td>X₁ 3·225</td>
</tr>
<tr>
<td>X₂ 2·265</td>
<td>X₂ 2·245</td>
</tr>
<tr>
<td>X₃ 1·145</td>
<td>X₃ 1·075</td>
</tr>
<tr>
<td>x₁ 1·435</td>
<td>x₁ 1·46</td>
</tr>
<tr>
<td>x₂ 1·01</td>
<td>x₂ 0·95</td>
</tr>
<tr>
<td>x₃ 0·515</td>
<td>x₃ 0·39</td>
</tr>
<tr>
<td>Z₁ 1·155</td>
<td>Z₁ 1·17</td>
</tr>
<tr>
<td>Z₂ 3·46</td>
<td>Z₂ 3·40</td>
</tr>
<tr>
<td>Z₃ -2·26</td>
<td>Z₃ -2·285</td>
</tr>
<tr>
<td>z₁ 0·51</td>
<td>z₁ 0·44</td>
</tr>
</tbody>
</table>
(2) Each carbon atom is roughly triangular, thus appearing to be definitely polarised in the direction of its appropriate chlorine atom and of the two neighbouring carbon atoms. No polarisation towards the centre of the benzene ring is indicated. On the other hand, there seems to be no corresponding polarisation of the chlorine atoms.

(3) Outside each chlorine atom there is a kind of buffer region of low electron density. It is probable, however, that these (20) contours would not appear if the Fourier series were completed and that they are part of a diffraction effect due to the termination of the series while the separate terms are still large.* Similarly, no reliance can be placed on the curious shape of the (20) contour within the benzene ring, unless it is found to be repeated in the analysis of other benzene derivatives.

Shape of the Molecule.

The positions of the Cl and C atoms, as given by the Fourier analysis, are most easily described in terms of polar co-ordinates.

<table>
<thead>
<tr>
<th>Chlorine atoms</th>
<th>Carbon atoms</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_1 = 2.985$</td>
<td>$r_1 = 1.32$</td>
</tr>
<tr>
<td>$\theta_1 = \pm 20^\circ 25'$</td>
<td>$\omega_1 = \pm 17^\circ 20'$</td>
</tr>
<tr>
<td>$R_2 = 3.115$</td>
<td>$r_2 = 1.325$</td>
</tr>
<tr>
<td>$\theta_2 = \pm 76^\circ 55'$</td>
<td>$\omega_2 = \pm 77^\circ 15'$</td>
</tr>
<tr>
<td>$R_3 = 2.935$</td>
<td>$r_3 = 1.26$</td>
</tr>
<tr>
<td>$\theta_3 = \mp 44^\circ 0'$</td>
<td>$\omega_3 = \mp 47^\circ 5'$</td>
</tr>
</tbody>
</table>

It will be seen from these numbers that the distances of the carbon atoms from the origin are about 8 per cent, less than was assumed in the first approximation. Neither they nor the chlorine atoms are arranged on a regular hexagon in the [010] projection.

The intensities of reflection from planes in zones other than the \{h0l\}, though incomplete, show conclusively that, unlike C₆(CH₃)₆, the atoms do not all lie in the one axial plane. As was explained in the paper on C₆(CH₃)₆, the consequence of any such arrangement of plane layers of atoms parallel to an axial plane would be that the structure factors of all planes \{hkl\} would be independent of one index. Thus, in the case of C₆(CH₃)₆ the structure factors for the series of planes \{h0l\} showed exactly the same variations as those for the series \{hk1\}, \{hk2\}, etc. Also, the (001) plane was an excellent reflector, and showed a "normal" falling off of intensities from its various orders; a further indication that the atoms were arranged in sheets parallel to that plane.

For C₆Cl₆ the (020) plane, as far as can be judged, is not a good reflector at

all, and the (040) intensity is less than would be expected for the "normal" falling off.

The following are the remaining "observed" structure factors, corrected for falling off of atomic scattering power with angle, etc., but not for absorption.

Table IV.

<table>
<thead>
<tr>
<th>(hkl)</th>
<th>S</th>
<th>(hkl)</th>
<th>S</th>
<th>(hkl)</th>
<th>S</th>
<th>(hkl)</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>110</td>
<td>128</td>
<td>112</td>
<td>50</td>
<td>002</td>
<td>100</td>
<td>112</td>
<td>79</td>
</tr>
<tr>
<td>220</td>
<td>28</td>
<td>224</td>
<td>&lt;21</td>
<td></td>
<td></td>
<td>224</td>
<td>&lt;20</td>
</tr>
<tr>
<td>330</td>
<td>&lt;21</td>
<td>336</td>
<td>&lt;22</td>
<td>1111</td>
<td>29</td>
<td>336</td>
<td>&lt;21</td>
</tr>
<tr>
<td>440</td>
<td>&lt;24</td>
<td>113</td>
<td>32</td>
<td>1110</td>
<td>41</td>
<td>111</td>
<td>48</td>
</tr>
<tr>
<td>111</td>
<td>30</td>
<td>226</td>
<td>&lt;21</td>
<td>110</td>
<td>49</td>
<td>225</td>
<td>34</td>
</tr>
<tr>
<td>222</td>
<td>24</td>
<td>114</td>
<td>58</td>
<td>118</td>
<td>&lt;19</td>
<td>333</td>
<td>&lt;21</td>
</tr>
<tr>
<td>333</td>
<td>&lt;22</td>
<td>228</td>
<td>&lt;21</td>
<td></td>
<td></td>
<td>444</td>
<td>&lt;24</td>
</tr>
</tbody>
</table>

Absorption maximum for (002).

| 002  | 100| 012  | 160| 020  | 64| 120  | 84|
| 015  | 43 | 024  | 45| 040  | <50| 240  | <39|
| 014  | 30 | 036  | <50|       |    | 122  | 58|
| 013  | 39 | 011  | 68| 212  | 50| 244  | <39|
| 022  | <45|       |    |       |    |       |    |

Many other planes in these zones were examined but no other reflections were found. The needle-like shape of the crystals, however, made measurements in any but the \{h0l\} zone exceedingly difficult.

The two centrosymmetrical molecules in the unit cell are reflections of one another in the (010) plane (fig. 8 (a)). If the component atoms all lay actually in that plane, the molecules would be, in effect, identical, and all planes \( \{hkl\} \) having \((k + l)\) odd would disappear (fig. 8 (b)).

This is quite obviously not the case, as the presence of such reflections as (112), (114), (012), etc., shows.

We are therefore faced with the further problem of finding the "y" parameters for all the atoms. Without more data this cannot be done, but certain general conclusions may be stated:—
(1) The projections of the C atom centres on the (010) plane lie on an ellipse, of semi-major axis 1·355 A., and semi-minor axis 1·26, the major axis making an angle of 51° 34′ with the crystallographic a axis.

(2) This projection is not compatible with any arrangement of the C atoms in a plane regular hexagon. There is, moreover, only one plane arrangement of C atoms, equidistant from one another, which would give the required projection. This plane ring, ABCA'B'C', shown in fig. 9, would be inclined to the (010) plane at an angle of 32° 20′, and would involve

\[ AB = BC' = AC = 1\cdot42 \text{ A.} \]
\[ OA = 1\cdot555 \quad OB = 1\cdot36 \quad OC = 1\cdot34 \]
\[ \angle AOC = 58° 20′ \quad \angle AOB = 58° 0′ \quad \angle BOC' = 63° 40′. \]
The plane of the ring would be tilted about the line PP', which makes an angle of 97° 40' with the a axis, and the y parameters would be

(A) \( y_1 = \pm 0.82 \) \hspace{1cm} (B) \( y_2 = \pm 0.295 \) \hspace{1cm} (C) \( y_3 = \pm 0.455 \).

Figs. 10 (a) and (b) show the projections of such a ring on the planes (100) and (001).

If the Cl atoms also lay in the same plane, then their Y parameters would be \( \pm 1.83, \pm 0.70, \pm 1.135 \) respectively, and the actual C—Cl distances would be 1.95, 1.835 and 1.81, giving a mean Cl radius of about 1.155.

(3) On the other hand, the projection on (010) might result from a puckered benzene ring for which

\[ AB = BC' = AC = 1.54 \text{ A.} \]

(A) \( y_1 = \pm 0.265 \) \hspace{1cm} (B) \( y_2 = \mp 0.545 \) \hspace{1cm} (C) \( y_3 = \mp 0.43 \).

Again the ring would be an irregular one, except for the constant distance apart of the atoms. The angles would not be tetrahedral, but only very approximately so (figs. 11 (a) and (b)).

(4) There are, of course, an infinite number of other possible arrangements, all of which would give the same projection on (010). No adequate means of deciding on the true arrangement are available at present.

It is, however, significant that the only plane ring which would account for the results, actually involves a C—C distance of 1.42 A., the distance found in graphite and in \( C_6\text{(CH}_3)6 \).

There is no possibility of a regular arrangement (either tetrahedral or co-planar) of the three carbon valencies, which at the same time preserves a constant interatomic distance either from carbon to carbon or from carbon to chlorine.
Cleavage.

The full contour diagram (fig. 6) readily explains the course of the cleavages. There are bands of low electron density between the molecules in directions parallel to (001), which is the best cleavage plane, and also parallel to (100) and (102), the secondary cleavage planes. The slipping on (111) is related to the tilt and general arrangement of the molecules relative to that plane, and cannot be explained from the limited data available.

Conclusions.

It is clear that the original intention of the research has not been adequately fulfilled. One projection of the molecule has been found with some certainty, but it is not possible to state whether the benzene ring in this compound is plane or not. If, however, it is plane, then the distance between adjacent carbon atoms in the ring must be 1.42 A. The distances from C to Cl atoms in the projection are 1.675, 1.665 and 1.79. These distances therefore constitute a lower limit for the actual C—Cl distances in the molecule.

Acknowledgments.

The writer's grateful thanks are due to the Council of Bedford College, London, for a scholarship enabling her to work in the Physics Laboratories of the University of Leeds; to the Royal Society for a grant covering the cost of some of the apparatus employed, and to the Managers of the Royal Institution for a subsequent grant which permitted the completion of the work.