

The Crystal Structure of the Epsilon Isomer of 1,2,3,4,5,6-Hexachlorocyclohexane

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The determination of the structure of this isomer of hexachlorocyclohexane is a part of the investigations of the cyclohexane derivatives, which are being carried out at the University of Oslo by O. Hassel and co-workers. The crystal structure and the configuration of the molecule have in this case been found directly from the X-ray data without any a priori assumptions about the mutual arrangement of the atoms.

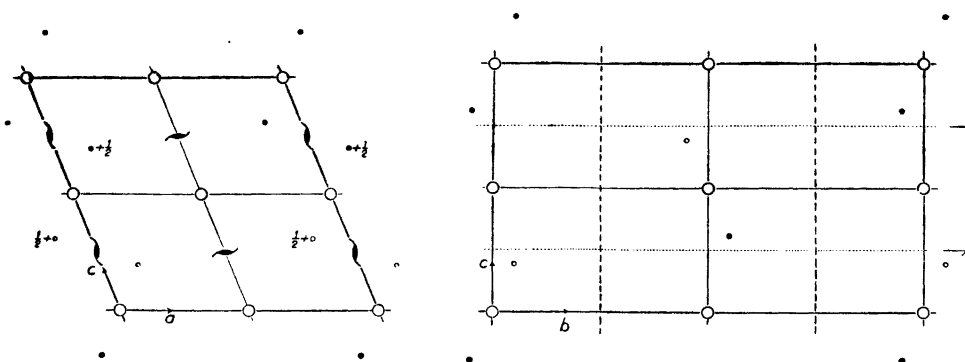
EXPERIMENTAL

The isolation of the epsilon isomer and crystallographic data for it have been described by Kauer, Du Vall and Alquist¹. The crystal system is monoclinic, and the unit cell contains two molecules. By means of rotation and Weissenberg photographs the dimensions of the cell were found to be $a = 7.02$ A, $b = 11.79$ A, $c = 6.80$ A and $\beta = 112^\circ$. The data given by Kauer *et al.*¹ are $a = 6.94$ A, $b = 11.66$ A, $c = 6.77$ A, $\beta = 111^\circ$. The space group is $C_{2h}^5 - P2_1/c$. The dipole moment of the molecule is said to be zero, a result which was confirmed by measurements carried out in Oslo².

In order to determine the intensities, two complete sets of Weissenberg photographs were taken, the first set by rotating the crystal about the a -axis, the second one by rotation about the b -axis. Unfiltered Cu-radiation was used, and the intensities, about 500 in all, were measured on an arbitrary scale by a visual comparison between the $K\alpha_1$, the $K\alpha_2$, the $K\alpha_1 + K\alpha_2$ and the $K\beta_1$ spots.

DETERMINATION OF THE PARAMETERS OF THE CHLORINE ATOMS

Figs. 1 a and b show the 4-fold position of the atoms $(x, y, z; \bar{x}, \bar{y}, \bar{z}; x, \frac{1}{2} + y, \frac{1}{2} - z; x, \frac{1}{2} - y, \frac{1}{2} + z)$ and the symmetry elements in the unit cell of



Figs. 1 a and b: Symmetry elements and equivalent positions in space group

$C_{2h}^5 - P2_1/c$

○ centre of symmetry

λ , - - - \rightarrow 2-fold screw axis

- - - - - glide plane

○, ● general positions of the atoms. ○ and ● signify $+y$ and $-y$ respectively in Fig. 1 a, $+x$ and $-x$ in Fig. 1 b.

the space group $C_{2h}^5 - P2_1/c$. As the crystal has a 2-fold screw axis parallel to the b -axis, the Patterson-Harker section $P(u, \frac{1}{2}, w)$ may be used to determine the projection of the atoms along this axis. The vector distance from the origin to a maximum in the synthesis $P(u, \frac{1}{2}, w)$ gives twice the vector distance of the corresponding atom from the screw axis. Further the presence of a glide plane gives the possibility to determine the projection of the atoms parallel the ac -plane on to the b -axis, as the distance of a maximum from the origin in the section $P(0, v, \frac{1}{2})$ gives twice the distance of the corresponding atom from the glide plane.

Figs. 2 and 3 show the sections $P(0, v, \frac{1}{2})$ and $P(u, \frac{1}{2}, w)$ respectively. We may only expect to find the 3 "space group" peaks (also named Harker peaks)³ due to the chlorine atoms. Fig. 2 in fact gives 3 well separated peaks. The positions correspond to:

$$2y_1 = 0.376 \quad 2y_2 = 0.260 \quad 2y_3 = 0.142$$

In Fig. 3, however, 6 peaks appear. Probably the 3 maxima labelled A, B and C correspond to "space group" peaks. First they are the highest ones and next they all lie close to the a -axis. The fact that all the maxima in the Patterson projections $P(u, w)$ and $P(v, w)$ (Figs. 4 and 5) have approximately

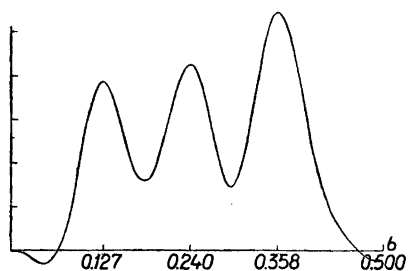


Fig. 2. Patterson synthesis $P(0, v, \frac{1}{2})$. The ordinates are given on an arbitrary scale. The same scale is used in all Patterson sections. The contours in the 2-dim. syntheses correspond to $P(u, v, w) = 1, 2, 3, \dots$

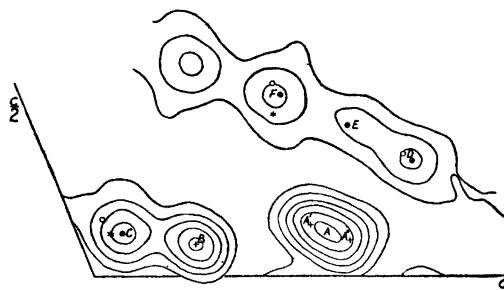


Fig. 3. Patterson synthesis $P(u, \frac{1}{2}, w)$. + denote chlorine space group peaks, O carbon space group peaks. * and ● denote peaks arising from vector distances between not symmetry-equivalent chlorine atoms and vector distances between chlorine and carbon atoms respectively, having v -values in the interval 0.5 ± 0.06 .

the w -values 0 and $1/2$ seems to indicate either that the “space group” peaks in Fig. 3 all lie close to the a -axis (giving z -values $\pm 1/4$), or are all near the line $w = 1/2$ (giving $z = 0$). The peaks labelled D, E and F in the same figure must in that case be due to Cl—Cl or Cl—C distances, where the vector separations parallel to b are close enough to $1/2$ for the peaks to appear in the distribution $P(u, \frac{1}{2}, w)$.

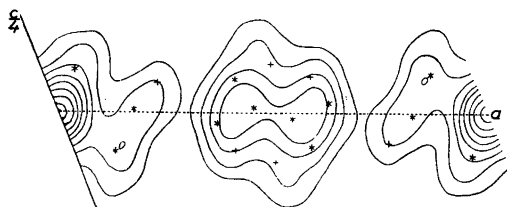


Fig. 4. Patterson projection on (010) . Contours are drawn at equal intervals on an arbitrary scale. + and * denote the system of vector peaks arising from the chlorine atoms, the frequency of the distances * being twice the distances +.

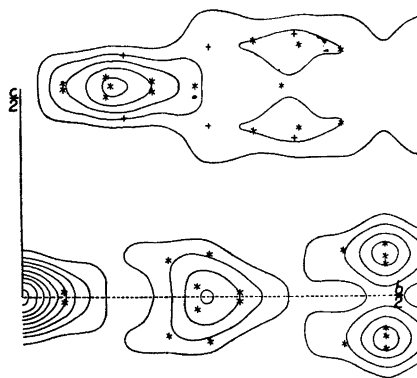
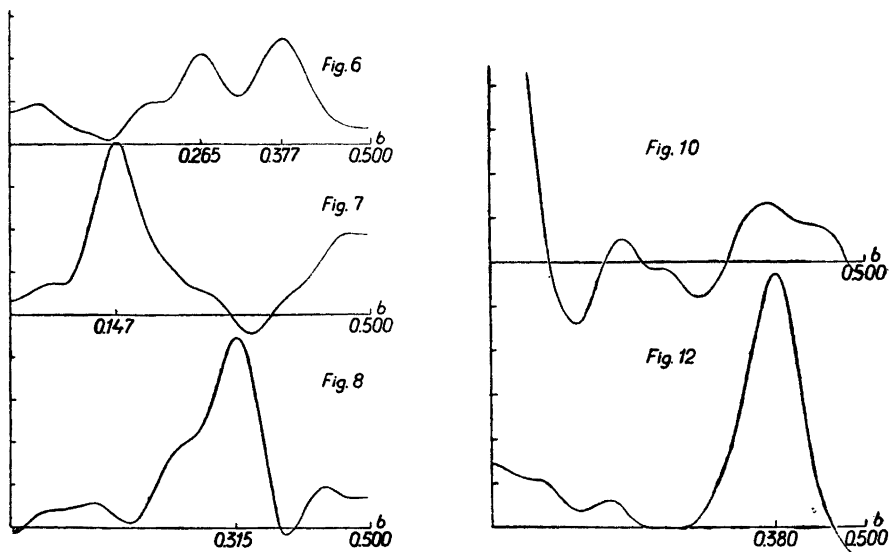


Fig. 5. Patterson projection on (100) . The contours and the crosses have the same meaning as in Fig. 4.



Figs. 6–8. Fig. 6 represents the Patterson synthesis $P(2x_A, v, 2z_A)$. Fig. 7 the synthesis $P(2x_B, v, 2z_B)$ and Fig. 8 the synthesis $P(2x_C, v, 2z_C)$.

Fig. 10 and 12. Fig. 10 represents the Patterson synthesis $P(0, v, 0)$, Fig. 12 the synthesis $P(x_{B_1} - x_{A_1}, v, z_{B_1} - z_{A_1})$.

If x_1, y_1, z_1 and $\bar{x}_1, \bar{y}_1, \bar{z}_1$ indicate the coordinates of two centrosymmetrical atoms, then the section $P(2x_1, v, 2z_1)$ must have a maximum in $v = 2y_1$. As a further check, the distribution in the sections $P(2x_A, v, 2z_A)$, $P(2x_B, v, 2z_B)$ and $P(2x_C, v, 2z_C)$ were calculated (A, B and C refer to the same letters in Fig. 3). The results are shown in Figs. 6, 7, and 8 respectively. The maxima in Fig. 6 have the positions $v = 0.265$ and $v = 0.377$. The maximum labelled A in Fig. 3 therefore consists of two overlapping “space group” peaks. The maximum at $v = 0.147$ in Fig. 7 confirms the assumption that B also forms a “space group” peak, whereas the big peak at $v = 0.315$ in Fig. 8 must be due to a vector distance between atoms which are not symmetry-equivalent.

Based upon the above discussion the possible xz -values of the chlorine atoms must be as indicated in Fig. 9. This projection is also named the implication diagram². In transferring the synthesis $P(u, \frac{1}{2}, w)$ to the implication diagram, a certain ambiguity is involved, since it is quite impossible to determine whether the peak labelled B in Fig. 3 implies the positions B_1, B_2, B_3, B_4 or B'_1, B'_2, B'_3, B'_4 , in Fig. 9, for example. To eliminate this ambiguity and thus obtain the real projection of the chlorine atoms, the following procedure has been adopted: The projection of 4 symmetry-equivalent atoms may of

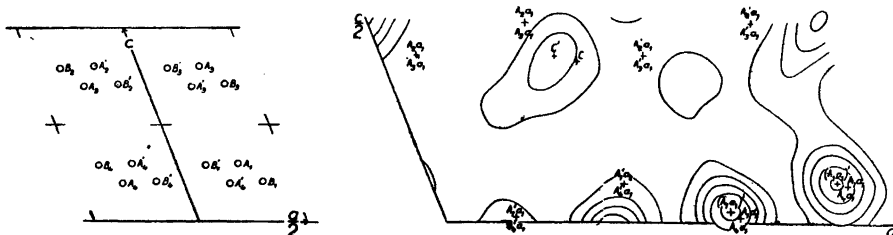


Fig. 9. Implication diagram for the 12 chlorine atoms on (010). (Possible projections of the chlorine atoms on (010).)

Fig. 13. Patterson synthesis $P(u, 1/4, w)$.

course be arbitrary chosen, as only the mutual arrangement of the atoms is of importance. For instance the projections labelled B_1, B_2, B_3 and B_4 in Fig. 9 may be chosen. If in the projection of the other 8 chlorine atoms pairs coincide, then the section $P(0, v, 0)$ must show a maximum. Fig. 10, representing the synthesis $P(0, v, 0)$ shows no maximum big enough to explain a Cl—Cl distance different from zero. (In this special section such a maximum should have a value 4 times a maximum in Figs. 6 and 7, or twice a maximum in Figs. 2 and 12.) However, the distribution in the section $P(x_{A1} - x_{A3}, v, z_{A1} - z_{A3})$ approximately given by $P(2x_C, v, 2z_C)$ in Fig. 8 [$P(x_{A1} - x_{A3}, v, z_{A1} - z_{A3}) = P(0.077, v, 0.608)$ and $P(2x_C, v, 2z_C) = P(0.107, v, 0.609)$] exhibits a maximum (at $v = 0.315$). The real projection of the 12 chlorine atoms is therefore given by $A_1, A_2, A_3, A_4, A'_1, A'_2, A'_3, A'_4, B_1, B_2, B_3, B_4$, in Fig. 9. The Patterson projection $P(u, w)$ (Fig. 4) also confirms this result, as there is a very good correspondance between the positions of calculated and experimental peaks.

The synthesis $P(0, v, \frac{1}{2})$ (Fig. 2) gave the y -parameters of the chlorine atoms. In this case there is no ambiguity, and the implication diagram (Fig. 11) is therefore equal to the projection of the atoms along the ac -plane on to the b -axis.

The relation between the xz -values and y -values can be determined in several ways. From Fig. 7 we know that there is a relation between the projections labelled B_1, B_2, B_3, B_4 (Fig. 9) and b_1, b_2, b_3, b_4 (Fig. 11). One combi-

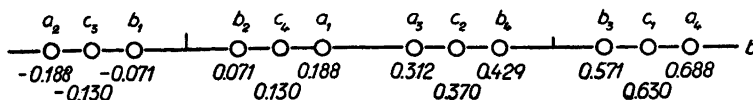


Fig. 11. Projection of the chlorine atoms on the b -axis.

nation may be made arbitrarily, *e.g.* B_1b_1 , and then the further relations B_2b_2 , B_3b_3 and B_4b_4 follow automatically. A combination of B_1 with b_2 , b_3 or b_4 would have given the same arrangement, the only difference being a translation of the origin to one of the other seven non-equivalent centres of symmetry in the unit cell. The y -value corresponding to the projection A_1 (Fig. 9) for instance, can be determined by means of the section $P(x_{B_3} - x_{A_1}, v, z_{B_3} - z_{A_1})$. This synthesis (Fig. 12) has a maximum at $v = \pm 0.380$, giving $y_{A_1} = 0.191$ or $y_{A_1} = -0.049$. The first value corresponds to the projection a_1 in Fig. 11 ($y_{a_1} = 0.188$), and we therefore have the relations $A_1a_1, A_2a_2, A_3a_3, A_4a_4$. Utilizing the approximations $P(u, y_{a_1} - y_{b_1}, w) \approx P(u, 1/4, w)$ and $P(u, y_{b_4} - y_{a_1}, w) \approx P(u, 1/4, w)$, the distribution in the section $P(u, 1/4, w)$ (Fig. 13) confirms the result just obtained. Crosses in Fig. 13 denote the position of the 8 peaks calculated when assuming the relations A_1a_1, A_2a_1 , a.s.o. The ambiguity is due to the position of the special plane $v = 1/4$ bisecting the distances between the two symmetry planes $v = 0$ and $v = 1/2$.

The relation between the projections A'_1, A'_2, A'_3, A'_4 (Fig. 9) and c_1, c_2, c_3, c_4 (Fig. 11) can easily be found from Fig. 8, as we have the approximation $P(x_{A_1} - x_{A'_3}, v, z_{A_1} - z_{A'_3}) \approx P(2x_C, v, 2z_C)$.

The maxima at ± 0.315 gives $y_{A'_3} = -0.127$ or $y_{A'_3} = 0.503$. Within the limits of error, the value $y_{A'_3} = -0.127$, is equal to y_{c_3} in Fig. 11 ($y_{c_3} = -0.130$), and we therefore find the remaining relations $A'_1c_1, A'_2c_2, A'_3c_3$ and A_4c_4 .

As a final confirmation of the correctness of the relations found between the xz - and the y -values, the system of vector peaks arising from the chlorine atoms are marked in the Patterson projection $P(v, w)$ (Fig. 5). The agreement between the positions of calculated and experimental peaks is very satisfactory.

The direct determination of the positions of the chlorine atoms has now been completed. The overlapping of the two "space group" peaks in Fig. 3, however, gives rise to an uncertainty in the determination of the correspond-

Table 1. The parameters of the atoms expressed as fractions of the corresponding lattice translation.

		x	y	z
Cl_1	$(Cl_{B_1b_1})$	0.369	-0.071	0.212
Cl_2	$(Cl_{A_1a_1})$	0.270	0.188	0.312
Cl_3	$(Cl'_{A_4c_4})$	-0.190	0.130	0.298
C_1		0.206	0.013	0.005
C_2		0.089	0.115	0.095
C_3		-0.035	0.041	0.177

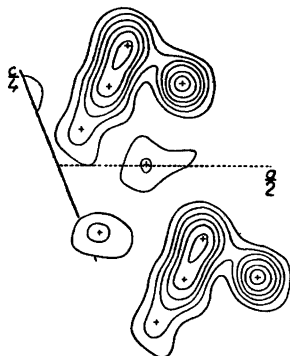


Fig. 14. Electron density projection along b -axis on (010) . Contours are drawn at intervals of 5 electrons per Å^2 .

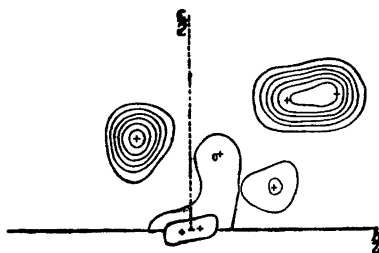


Fig. 15. Electron density projections along a -axis on (100) . Contours are drawn at intervals of 5 electrons per Å^2 .

ing x , z -values. To obtain more correct values, the peaks labelled A_1a_1 and C in Fig. 13 were utilized. The last peak is due to the vector distance $(2x_{A_1}, 2y_{A_1}, 2z_{A_1}) \approx (2x_{A_1}, 1/4, 2z_{A_1})$. The resulting parameters are given in Table 1, and the corrected positions of the "space group" peaks in Fig. 3 are labelled A' and A'' , the corrected positions of the peaks in Fig. 13 (A_1a_1)' and C'' . The probable error in the parameters may be about $\pm 0.03 \text{ Å}$.

DETERMINATION OF THE POSITION OF THE CARBON ATOMS

Fig. 14 shows a Fourier projection along the a -axis, Fig. 15 a Fourier projection along the b -axis. The signs of the observed $F(hkl)$ values were obtained by calculating the structure factors for the chlorine atoms only. After the positions of the carbon atoms have been fixed, a re-calculation of the structure factors for the chlorine and the carbon atoms shows that only

Table 2. Intramolecular distances given in Ångström units (see Figs. 16 and 17).

$\text{Cl}_1 - \text{Cl}_2 = 3.27 (3.21)$	$\text{C}_1 - \text{C}_2 = 1.71 (1.54)$
$\text{Cl}_2 - \text{Cl}_3 = 3.26 (3.21)$	$\text{C}_2 - \text{C}_3 = 1.48 (1.54)$
$\text{Cl}_3 - \text{Cl}_4 = 3.28 (3.21)$	$\text{C}_3 - \text{C}_4 = 1.50 (1.54)$
$\text{Cl}_1 - \text{Cl}_3 = 4.80 (4.71)$	$\text{C}_1 - \text{C}_4 = 2.89 (2.95)$
$\text{Cl}_2 - \text{Cl}_4 = 4.76 (4.71)$	$\text{C}_2 - \text{C}_5 = 3.06 (2.95)$
$\text{Cl}_3 - \text{Cl}_5 = 5.47 (5.44)$	$\text{C}_3 - \text{C}_6 = 2.79 (2.95)$
$\text{Cl}_1 - \text{Cl}_4 = 5.17 (5.02)$	$\text{C}_1 - \text{Cl}_1 = 1.75 (1.79)$
$\text{Cl}_2 - \text{Cl}_5 = 6.32 (6.32)$	$\text{C}_2 - \text{Cl}_2 = 1.76 (1.79)$
$\text{Cl}_3 - \text{Cl}_6 = 6.39 (6.32)$	$\text{C}_3 - \text{Cl}_3 = 1.90 (1.79)$

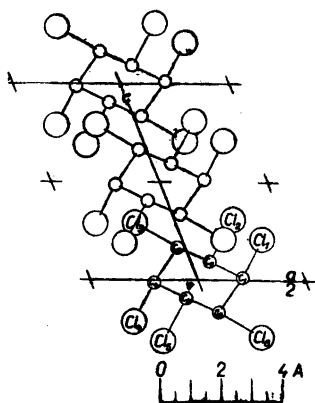


Fig. 16. Arrangement of atoms in the *b*-axis projection.

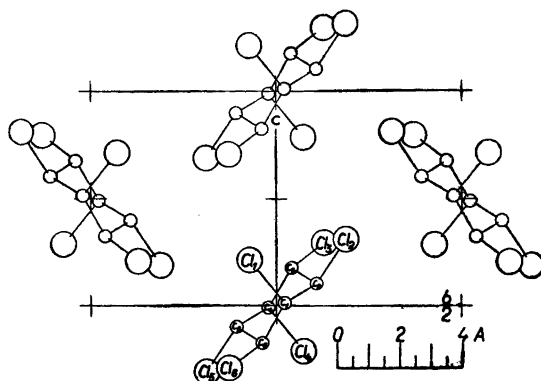


Fig. 17. Arrangement of atoms in the *a*-axis projection.

4 out of 95 reflections used, would have the wrong sign, and these, having very small F -values, would have a negligible effect on the position of the centres of the peaks. In Figs. 14 and 15, both the chlorine as well as the carbon atoms appear clearly. For two of the chlorine atoms, the resolution in both projections is so poor that the parameters cannot be determined. Within the assumed limits of error, the values $x = 0.366$, $z = 0.214$ and $dy = -0.072$, $z = 0.211$ for the third chlorine atom agree with the parameters already found. The parameters of the carbon atoms are given in Table 1. Owing to overlapping, diffraction effects and errors in the intensity measurements, great accuracy in the parameters cannot be expected. The errors may possibly be ± 0.1 Å.

It is now possible to explain the extra peaks appearing in the various sections of $P(u, v, w)$. However, consideration will be confined to recording the positions of the "space group" peaks calculated for the carbon atoms in Fig. 3, and also in the same figure the peaks due to Cl—C distances having vector separations parallel to the *b*-axis in the interval $v = 0.5 \pm 0.06$.

DESCRIPTION OF THE STRUCTURE

Figs. 16 and 17 give the projections of the structure along the *a*- and *b*-axis. The smallest calculated distances between two chlorine atoms belonging to different molecules, are 3.74 Å, 3.76 Å and 3.89 Å. In the molecule the carbon atoms form a puckered sixmembered ring, the chlorine atoms being in the

positions $\epsilon\kappa\kappa\epsilon\kappa\kappa$. The same result was previously obtained by Bastiansen, Ellefsen and Hassel⁴. Using the electron diffraction sector method, they showed that the molecule had this configuration in the vapour state. Table 2 gives the calculated intramolecular distances derived from the parameters in Table 1. The corresponding calculated distances based on a model of the molecule where the C—C distance is 1.54 Å, the Cl—C distance 1.79 Å and the valency angle equal to 109.5°, are added in brackets in the same table. Unfortunately, the inaccuracy in the parameters of the carbon atoms makes it impossible to attach any importance to the deviation between the theoretical and experimental C—C and C—Cl distances. However, the average distance of 3.27 Å as compared with 3.21 Å calculated between two chlorine atoms and especially the comparatively great difference of 0.15 Å between the theoretical and experimental value for the 1 ϵ , 4 ϵ chlorine distance, seem to indicate a certain deformation of the molecule.

SUMMARY

The crystal structure of the epsilon isomer of 1,2,3,4,5,6-hexachlorocyclohexane has been determined from X-ray data only. The parameters of the chlorine atoms were derived from one- and two-dim. Patterson syntheses. Two-dim. Fourier projections were used to determine the coordinates of the carbon atoms. The investigations show that the carbon atoms in the molecule form a puckered six-membered ring, the chlorine atoms being in the positions $\epsilon\kappa\kappa\epsilon\kappa\kappa$.

In conclusion I want to express gratitude to Dr. L. K. Frevel, Midland, Mich., U.S.A. for placing the substance at our disposal and to Prof. O. Hassel in Oslo for suggesting the problem and for helpful criticism of the text of this paper. I also wish to thank Prof. G. Hägg in Uppsala for enabling me to carry out the experimental part of the investigations during a visit to his laboratory.

LITTERATUR

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