equally well be accounted for if, instead, we considered chlorine atoms as occupying a corner of the symmetry-bound tetrahedron around the same (*b*) points and swinging from one corner to the other. Although experimental data at our disposal are not sufficient to warrant a decision between these two versions, the Fourier projection of electron density of high-boracite (Fig. 2) is rather suggestive of the latter picture. The contour around chlorine atoms (overlapped by magnesium atoms in (100) projection) indicates conspicuous lumps just where chlorine atoms might be temporarily stationed in their swinging motion.

Should this be the real state of affairs, the α–β inversion would be adequately explained as due to the moving chlorine atoms simply coming to a standstill. At the transition temperature chlorine atoms may not shift from one definite position to another as we conceive ordinarily. It would be, indeed, difficult to understand why the inversion is accompanied by no observable effect on the lattice dimensions if a change in positions of certain atoms, and of their environment, had actually taken place.

References

BECKENKAMPF, J. (1933). *Hintze's Handbuch der Mineralogie*. Leipzig: Veit.

COHN, W. M. (1928). *Z. Phys.* **50**, 124.

FRIEDEL, G. (1904). *Étude sur les Groupements cristallins.* Saint-Étienne: Thomas.

FRIEDEL, G. (1926). *Leçons de Cristallographie.* Paris: Berger-Levrault.

International Tables for the Determination of Crystal Structures (1935). Berlin: Borntraeger.

ITO, T. (1938). *Z. Krystallogr.* **100**, 437.

ITO, T. (1950). *X-ray Studies on Polymorphism.* Tokyo: Maruzen.

MEHMEL, M. (1934*a*). *Z. Krystallogr.* **87**, 239.

MEHMEL, M. (1934*b*). *Z. Krystallogr.* **88**, 1.

SOSMAN, R. B. (1924). *Properties of Silica.* New York: Chemical Catalog Co.

Acta Cryst. (1951). **4**, 316

The Crystal Structure of a Pentachlorocyclohexene, $C_6H_5Cl_5$

BY R. A. PASTERNAK*

University College, London W.C. 1, *England*

(*Received* 26 *October* 1950)

The crystal structure of a pentachlorocyclohexene, prepared from the δ-isomer of $C_6H_6Cl_6$ by treatment with alkali, has been determined by Fourier projections, lines and selected sections. The position of the double bond has been fixed unambiguously. The steric course of elimination in the case of δ-$C_6H_6Cl_6$ has been established by this investigation.

Introduction

In the course of an extended investigation on the kinetics of olefin elimination from the isomers of hexachlorocyclohexane (Hughes, Ingold & Pasternak, unpublished; see also Cristol, 1945) intermediate products of the formula $C_6H_5Cl_5$ could be isolated in the case of the γ- and δ-isomers. Whereas the former was obtained as a viscous liquid, the latter crystallized from petrol ether. In order to clarify the steric course of elimination the X-ray analysis of this compound was undertaken.

Physical and X-ray data

$C_6H_5Cl_5$ (m.p. 69° C.) is very soluble in organic solvents. It crystallizes from light petrol ether in conglomerates of badly developed crystals, which are suitable neither for optical nor for X-ray measurements. Single crystals, however, occasionally appear at the wall of the crystallization flask as thin plates. Under the polarizing microscope they show a very high birefringence and are biaxial negative. The principal index, β, lies in the plane of the plate; the other two are inclined to it. From the X-ray measurements it was found that the crystals were monoclinic, the *b* axis being parallel to β. The face of the plate was chosen as (001).

Samples for the X-ray investigations were prepared by cutting such plates by a razor blade down to about equal dimensions (0·01–0·03 cm.). They were mounted in lithium borate tubes, as they deteriorated in the open air. Most of them were distorted and had to be rejected, but ultimately some fairly good crystals were found.

The unit-cell dimensions, determined from rotation and Weissenberg photographs, are

$$a=7{\cdot}54,\quad b=18{\cdot}2(8),\quad c=7{\cdot}01\text{ A.};\quad \beta=105{\cdot}(1)^\circ.$$

Density (calculated for four molecules per unit cell), 1·811 g.cm.$^{-3}$; density (measured), 1·80 g.cm.$^{-3}$. Reflexions ($0k0$) and ($h0l$) are missing for k and h odd, respectively. The space group is therefore $P2_1/a$.

Weissenberg photographs were made of the ($0kl$)–($3kl$), ($hk0$)–($hk3$), ($h0l$)–($h6l$) layer lines with Cu $K\alpha$ radiation, using the multiple-film technique. The relative intensities were estimated visually. They were corrected for Lorentz, polarization and inclination

---

* Present address: California Institute for Technology, Pasadena, California, U.S.A.

factors. No absorption correction was applied: it would have been difficult on account of the irregular shape of the samples, and it seemed unimportant because of their small size. This was verified by comparing the relative intensity of a number of identical reflexions from two different crystals and from different layer lines also. The small size of the crystals, however, had the disadvantage of reducing the intensity of the photographs. An intensity range of not more than 1–500 could be realized with exposures of 30–60 hr.

Structure analysis

The analysis of such a structure may in principle be rather difficult, because the way in which the five heavy atoms of the molecule can be arranged in space is very little restricted. However, the knowledge of the structure of its mother substance, δ-$C_6H_6Cl_6$ (Bastiansen, Ellefsen & Hassel, 1949; Bijvoet, private communication), combined with theoretical arguments on the mechanism of elimination (Hughes, Ingold, Dhar, Mandour, Maw & Woolf, 1948), made an approximately planar arrangement of the atoms probable. Furthermore, the orientation of the molecule was indicated by the fact that the $(20\bar{1})$ reflexion was by far the strongest of all those observed and was, in addition, accompanied by a pronounced diffuse spot in Laue photographs. These facts pointed to a layer structure parallel to this plane (Lonsdale, 1941), an interpretation confirmed by the Patterson projection on (010), which consisted of rather sharp, high ridges along the $(20\bar{1})$ planes with deep valleys between them. Also, the arrangement of the four molecules in the unit cell was now quite obvious, taking into consideration the dimensions of the cell. They lay two by two in the $(20\bar{1})$ planes or in planes half-way between these, lined up along the b axis.

It seemed most promising to begin the detailed analysis with the (100) projection. This projection represents the molecule seen nearly perpendicular to its plane, because the (100) and $(20\bar{1})$ planes are almost equally inclined to the a axis (75 and 73°). An important advantage of this view is its small sensitivity to distortion of the molecule caused by the double bond. Thus one can assume as first approximation that one has to do with the flat, saturated compound. One may of course also expect the best resolution in this projection, at least if no overlapping of atoms from different molecules occurs.

Actually it was possible to fit a flat molecule into the (100) Patterson map in such a way that *ortho* chlorine atoms lay on lines nearly parallel to the c axis. No other position agreed satisfactorily with the complex peaks. With this result as starting point, approximate co-ordinates were found without difficulty by trial and error. The structure factors were calculated by using the simple device of Vand (1948). Already the first Fourier synthesis, made with about 40 terms, showed clearly the entire molecule. Three chlorine atoms were well resolved and four carbon atoms were indicated. However, the two remaining chlorine atoms overlapped with their counterparts from a second molecule, and the two carbon atoms were also masked by another molecule. After two consecutive syntheses this projection was abandoned for the time being, as no better resolution could be obtained and refinement became more difficult.

The (001) projection proved to be much more involved, as the molecule is seen sideways, possible distortions being most pronounced in this view. The peaks in the Patterson projection were of course very complex and could not be interpreted. Direct trial-and-error methods, too, did not give the right answer, partly because the carbon atoms were neglected in the calculation of the structure factors, their positions being very uncertain. This made the agreement between measured and calculated structure factors very poor for some important low-order reflexions, even in nearly correct trials. At last, three-dimensional Patterson line syntheses parallel to the a axis were undertaken through the end-points of those Cl–Cl vectors which promised to give clear maxima. They led unambiguously to one set of co-ordinates, surprisingly near to the final values, the maximum deviation being only 0·08 A. (An ordinary Harker–Patterson section in $y=\frac{1}{2}$ would not have given good resolution for this layer structure parallel to b.)

The signs of the stronger ($hk0$) reflexions were now determined and a Fourier synthesis was made. The chlorine atoms were all well resolved, whereas the carbon atoms masked each other completely, the plane of the ring being seen at too small an angle. As it was of special interest to locate the carbon atoms as well, this projection was not refined further, but immediately some three-dimensional work was initiated. The signs of the structure factors of important general reflexions were determined, still neglecting the carbon atoms. As the atoms all lie near to $(20\bar{1})$, a simple transformation of co-ordinates was carried out to make this the (100) plane, and a bounded section was calculated (Booth, 1948) parallel to it within the boundaries $x=\pm\frac{1}{10}$. All atoms but one chlorine atom were included and clearly resolved, and thus approximate y and z parameters for all of them were found. Line syntheses parallel to a through their centres gave the x parameters also.

With this complete set of co-ordinates all structure factors were calculated, this time taking also the carbon atoms into account. Before going further, the (100) projection was completed (Fig. 1).

As no mechanical calculating device was available, the three-dimensional refinement consisted only in one single section parallel to (010) through the centre of each atom, followed by a line synthesis parallel to b.*

---

* Booth's method of projected sections (Booth, 1948, pp. 40, 43), which was very tempting at first sight, turned out to be useless, as its hidden principal assumption is never fulfilled in a real case. It implies that only this section, which is supposed to go through the atom, has a positive electron density around the atom in the projection, and all other sections show there an electron density exactly equal to zero.

In the case of one carbon atom a difference of about 0·3 A. was found between the y co-ordinate taken for the section and that obtained from the line synthesis. The section was therefore recalculated at the new value of the parameter. The change in the x and z co-ordinates amounted to 0·04 and 0·02 A. respectively. As the other sections were all placed within 0·15 A. from the final y parameter, it was not found necessary to repeat them. Finally, doubtful structure factors were redetermined and the sections and lines corrected for the few changed signs. In Fig. 2 the sections through the carbon atoms are reproduced. As may be noticed, the peaks are on the whole fairly circular.

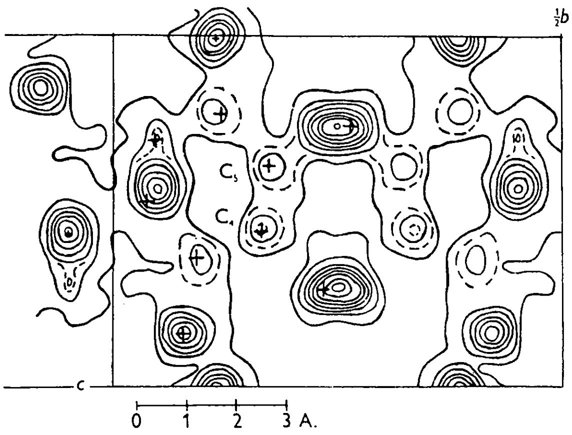

Fig. 1. Electron density projected on (100). Contours at intervals of about 4 e.A.$^{-2}$ for the chlorine atoms and 2 e.A.$^{-2}$ for the carbon atoms. Lowest contour at 2 e.A.$^{-2}$. The crosses indicate the final atomic positions.

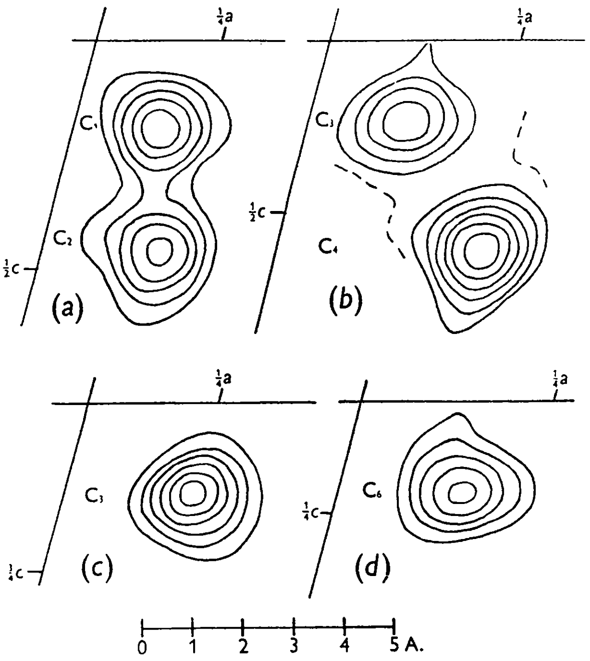

Fig. 2. Fourier sections parallel to (010) through the carbon atoms. Contours at intervals of about 1 e.A.$^{-3}$. Lowest contour at 2 e.A.$^{-3}$. The y co-ordinates of the sections are: (a) 0·042, (b) 0·166 (broken line at 1 e.A.$^{-3}$), (c) 0·093, (d) 0·114.

The measured and the calculated structure factors for the ($hk0$) and the ($0kl$) reflexions gave for the quantity $\Sigma\,|\,F_{\text{obs.}}-F_{\text{calc.}}\,|/\Sigma\,|\,F_{\text{obs.}}\,|$ values of 0·200 for the ($hk0$) and 0·185 for the ($0kl$) reflexions.

The average accuracy of atomic parameters (Table 1) is estimated to be about 0·02 A. for each co-ordinate of the chlorine atoms. For the carbon atoms an error up to 0·05 A. may be reasonable.

Table 1. *Atomic parameters*

	x/a	y/b	z/c
Cl_2	0·276	−0·053	0·566
Cl_3	0·448	0·079	0·848
Cl_4	0·237	0·235	0·727
Cl_5	0·125	0·265	0·258
Cl_6	−0·038	0·115	0·006
C_1	0·201	0·048	0·297
C_2	0·240	0·040	0·476
C_3	0·246	0·094	0·635
C_4	0·272	0·167	0·556
C_5	0·125	0·174	0·369
C_6	0·164	0·122	0·220

Discussion of the structure

In Fig. 3 the arrangement of the atoms and the bond lengths are given. The Cl–C distances are as a whole somewhat too long and the C–C distances too short compared with the standard values. Probably these deviations are not real, but originate mostly from the inaccuracy in the parameters of the carbon atoms. One would have expected, however, a random distribution of the errors.

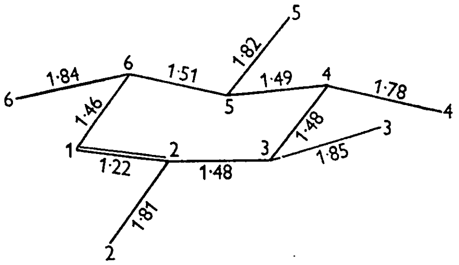

Fig. 3. Model of the molecule. Bond lengths are given in Ångström units.

Other important distances are those between chlorine atoms in the *ortho* position:

3·17 for Cl_2–Cl_3, 3·27 for Cl_3–Cl_4,
3·21 for Cl_4–Cl_5 and 3·32 A. for Cl_5–Cl_6.

The nearest intermolecular Cl–Cl distance was 3·55 A.

The double bond can be located with certainty between C_1 and C_2. It is not only the short bond length which indicates it, but also the fact that in the common section through both atoms the electron density between them is much higher than in a similar section through C_5 and C_6 (see Fig. 2(a) and (b)). This difference is believed to be real. The bond angles also point to the same thing (Table 2). The angles at the bond C_1–C_2 have values around that expected at a double bond, whereas all other bond angles are nearer to the tetrahedral angle. Finally, the atoms Cl_2, C_1, C_2, C_3 and C_6 lie approximately in one plane, the biggest deviation being 0·04 A. (Table 3). The atoms C_4 and C_5, which are not expected to be in the plane, are actually much farther away from it. The plane has been chosen so as to go through Cl_2 and to give the least-square deviation for the four carbon atoms.

Table 2. *Bond angles*

Cl_2–C_2–C_3	113°	C_2–C_3–C_4	107°
Cl_3–C_3–C_4	106	C_3–C_4–C_5	106
Cl_3–C_3–C_2	110	C_4–C_5–C_6	108
Cl_4–C_4–C_5	108	C_5–C_6–C_1	113
Cl_4–C_4–C_3	111		
Cl_5–C_5–C_6	106	Cl_2–C_2–C_1	117
Cl_5–C_5–C_4	112	C_6–C_1–C_2	118
Cl_6–C_6–C_1	107	C_1–C_2–C_3	130
Cl_6–C_6–C_5	110		

Table 3. *Distances of the atoms from the plane of the molecule*

Cl_2	C_1	C_2	C_3
0	+0·00(7)	+0·04(4)	−0·01(2)
C_6	C_4	C_5	Cl_3
−0·01(4)	+0·33(7)	−0·39(6)	+1·18(2)
Cl_4	Cl_5	Cl_6	
+0·08(8)	+0·06(2)	−1·25(3)	

+ = above; − = below the plane.

The steric relation between our compound and its mother substance δ-$C_6H_6Cl_6$ can now be seen readily. The latter has the structure shown in Fig. 4. When it is treated with alkali, Cl_1, the only chlorine atom in an ϵ-position (Bastiansen *et al.* 1947) is removed together with a proton from C_2 (or from the equivalent atom C_6). Simultaneously with the formation of the double bond, C_2 and Cl_2 have to move in one plane with C_1, C_3 and C_6, as is possible without large displacements of these atoms. The bond angles would assume the values 121° at C_1, 123° at C_2 and 116° at C_3, if a movement of C_2 took place alone. However, some adjustments must also occur, because the distance between Cl_2 and Cl_3 would get very short (2·89 A.). Thus the C_1–C_6 and the C_2–C_3 bonds are twisted, so as to lower Cl_6 and to lift Cl_3 relative to the plane of the molecule. By these displacements the distances Cl_5–Cl_6, Cl_3–Cl_4 and especially Cl_2–Cl_3 are increased. The twist undoubtedly also causes a movement of C_4 and C_5. Nevertheless, the relative atomic positions within the group Cl_4–C_4–C_5–Cl_5 seem to remain unchanged, as the distance Cl_4–Cl_5 is approximately the same as expected for the undistorted structure (3·18 A.).

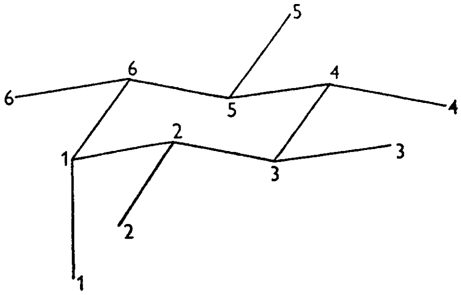

Fig. 4. Model of δ-$C_6H_6Cl_6$.

As for smaller displacements, however, and especially for possible distortions of bond angles, the present results are not accurate enough to be conclusive. A more exact X-ray analysis of a simpler derivative of cyclohexane would be desirable to clarify it.

This investigation has been carried out partly under a grant from 'Stiftung für Stipendien auf dem Gebiet der Chemie, Basel (Schweiz)'. The author wishes to express his gratitude to Prof. K. Lonsdale, University College, London, for introducing him to the technique of X-ray structure analysis and for hospitality in her laboratory, and to Prof. A. Tovborg-Jensen, Landbohøjskolen, Copenhagen, for permission to continue the investigation in his department.

References

Bastiansen, O., Ellefsen, O. & Hassel, O. (1949). *Acta chem. Scand.* **3**, 918.

Booth, A. D. (1948). *Fourier Technique in X-Ray Organic Structure Analysis.* Cambridge University Press.

Cristol, S. J. (1945). *J. Amer. Chem. Soc.* **69**, 338.

Hughes, E. D., Ingold, C. K., Dhar, M. L., Mandour, A. M. M., Maw, G. A. & Woolf, L. J. (1948). *J. Chem. Soc.* p. 2093.

Lonsdale, K. (1941). *Proc. Roy. Soc.* A, **177**, 272.

Vand, V. (1948). *J. Sci. Instrum.* **25**, 352.