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The Crystal Structure of Tetrachlorocyclohexane, M.P. 174° C.

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Following electron diffraction measurements of the vapour of tetrachlorocyclohexane of m.p. 174° C., a crystal-structure determination of the substance was carried out. The crystals are orthorhombic pseudotetragonal with two molecules in the unit cell. The space group is D_2^3–$P2_12_12$. Fourier projections of the structure in the planes (001) and (010) are given. The configuration of the molecule is 1ϵ, 2ϵ, 4κ, 5κ. Some deviations from an 'ideal' structure with tetrahedral valency angles are observed.

The direct chlorination of cyclohexane in strong light at ordinary temperature yields crystals of a tetrachlorocyclohexane melting at 174° C. (Sabatier & Mailhe, 1903). The structure formula of this compound has never been elucidated. We have observed, however, that the chlorination both of chlorocyclohexane and of 1,2-dichlorocyclohexane under the conditions just mentioned leads to the formation of the same compound. It therefore seems very probable that at least *two* of the chlorine atoms of the tetrachloro-compound are in 1,2-positions.

The investigation of the molecular structure of the tetrachlorocyclohexane was taken up a few years ago in our laboratory using the electron diffraction sector method. From the photometer records first obtained distribution curves were computed by H. Viervoll. Later on S. Furberg, on the basis of this and new material, analysed the $\sigma(r)/r$ curves in all details and was led to the following conclusions: (1) The six-membered carbon ring has the symmetrical 'chair' form. (2) No carbon atom is directly bonded to more than *one* chlorine atom. (3) The molecule contains both ϵ and κ (Hassel, 1943) C–Cl bonds.

The analysis of the scattering of electrons by the vapour left three structure alternatives open for further discussion:

(*a*) 1ϵ, 2ϵ, 4κ, 5κ; (*b*) 1κ, 2κ, 3κ, 5ϵ; (*c*) 1κ, 2ϵ, 3ϵ, 5κ.

It is interesting to note a further conclusion drawn by Furberg: if the structure corresponds to (*a*), then the two ϵ C–Cl bonds must be bent away from the principal axis of the carbon ring, the angle between a C–Cl bond and the axis being about 7°.

The dipole moment of the tetrachloro-compound was measured in our laboratory by Hetland (1948), who found $\mu = 2{\cdot}36$ D. This value nearly corresponds to that of the 1ϵ, 2ϵ, 4κ, 5κ-tetrabromocyclohexane, the structure of which was determined more than ten years ago (Halmøy & Hassel, 1939).

In order to decide between the three structures (*a*), (*b*) and (*c*) a crystal-structure analysis was carried out. The crystals obtained from solution generally show poor development, a substance built up of very thin fibres being the result of a crystallization. We finally succeeded, however, in obtaining needles (from chloroform) suited for X-ray examination. From rotation and Weissenberg photographs the dimensions of the orthorhombic (pseudotetragonal) unit cell were determined:

$$a = 7{\cdot}60,\quad b = 7{\cdot}54,\quad c = 7{\cdot}72\ \text{A}.$$

The correspondence with the data of the 1ϵ, 2ϵ, 4κ, 5κ-tetrabromo-compound (Halmøy & Hassel, 1939) is striking. The density of the crystals is 1·64 g.cm.$^{-3}$ (Sabatier & Mailhe, 1907) and the number of molecules in the unit cell therefore 2. The absence of reflexions (h00) and (0k0) with h and k odd also unambiguously leads to the same space group D_2^3–$P2_12_12$. The molecule must therefore possess a twofold symmetry axis, a fact which excludes the two alternatives (*b*) and (*c*) compatible with the electron-diffraction results. This might in itself be regarded as a definitive proof of the molecular configuration 1ϵ, 2ϵ, 4κ, 5κ. We have preferred, however, to determine the crystal structure in some detail, beginning with the projection of the structure in the (001) plane. With the help of the intensities of reflexions (hk0), and on the basis of an 'ideal' model with tetrahedral valency angles, approximate x and y values for the C and Cl atoms were computed, and in that way preliminary signs for the structure amplitudes were obtained. Two successive sets of two-dimensional Fourier syntheses referring to the xy plane were then carried out. In the first set only the reflexions having small h and k values were considered, and in this way preliminary values of x and y were found, allowing us to decide with certainty the signs of amplitudes corresponding to greater h and k values. The electron-density map corresponding to the xy projection and based upon all observed (hk0) reflexions is reproduced in Fig. 1.

In order to determine the z parameters, a corresponding electron-density map referring to the xz plane seemed especially well suited. Here also a preliminary structure, not an 'ideal' one, but a structure based on the x and y co-ordinates already obtained, was of great help for the determination of the signs of structure amplitudes. The resulting Fourier map is reproduced in Fig. 2. Fig. 3 shows projections of the structure both in the xy and in the xz plane, atomic centres only and the lines corresponding to valency bonds being indicated.

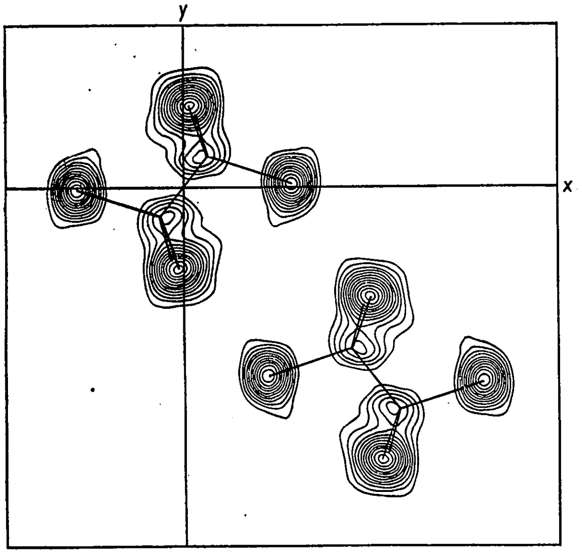

Fig. 1. Projection of the electron density in the (001) plane. x and y co-ordinates correspond to fractions of the lattice constants.

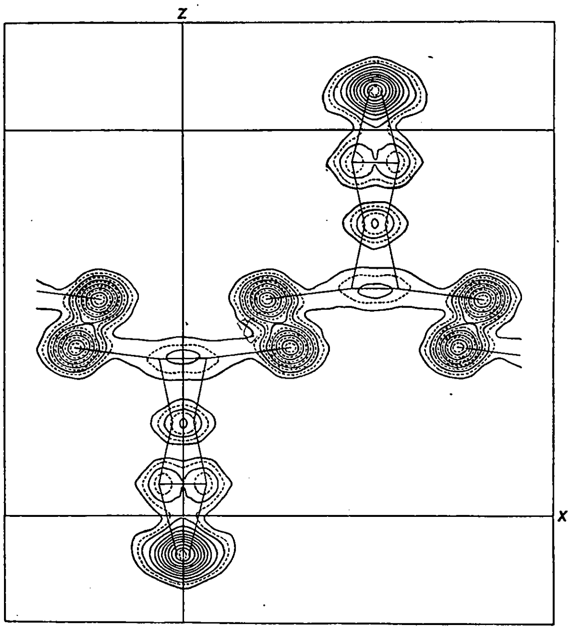

Fig. 2. Projection of the electron density in the (010) plane. x and z in fractions of the lattice constants. Every second contour line is dotted, the dotted lines being omitted at the high peaks resulting from nearly coincident chlorine atoms.

The positions of the Cl atoms were obtained from the maps by determining the intersection of the contour lines with planes parallel to the planes (100), (010) and (001) in the vicinity of the peaks, and drawing smooth curves through the points thus obtained. The carbon peaks are less accentuated and partly overlapped by other peaks, and the localization of the C atoms was therefore not carried out using the procedure just mentioned. We have assumed the carbon ring to have the classical 'chair' form and the C–C distance to be 1·54 A. The mean value of the C–Cl bond distance thus

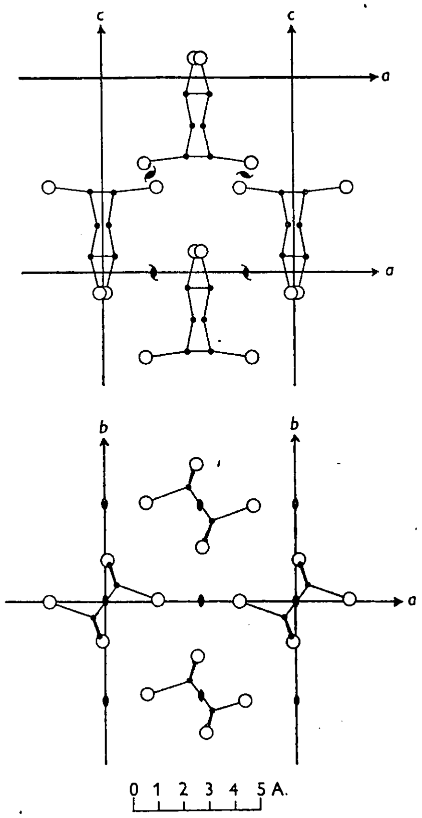

Fig. 3. Projections of the structure in the (010) plane (upper part) and in the (001) plane (lower part). Length of axes corresponding to Ångström units.

obtained is 1·79 A., in full agreement with the results of the electron-diffraction investigation. The co-ordinates of the Cl and C atoms are given in Table 1.

Table 1. *Co-ordinates of* C *and* Cl *atoms*

	x	y	z
Cl_1	0·282	−0·008	0·437
Cl_5	0·015	−0·215	−0·105
C_1	0·062	−0·081	0·408
C_5	0·062	−0·081	0·082
C_6	0·028	−0·194	0·245

It is easily recognized that the structure of the tetrachlorocyclohexane molecule corresponds to the 1ϵ, 2ϵ, 4κ, 5κ configuration, and that small deviations from the 'ideal' structure occur. These deviations are most strikingly demonstrated by the fact that the two ϵ C–Cl bonds belonging to the same molecule are not strictly parallel (compare Figs. 2 or 3). These bonds are both bent away from the principal axis of the carbon ring, obviously because of the repulsive forces between the ϵ chlorine atoms and the two nearest (ϵ-) H atoms. The angle between the C–Cl direction and the carbon ring axis is found to be about 7°, in full agreement with the result obtained by the electron diffraction method.

The intensity data were obtained from Weissenberg equator photographs with rotation about [001] and [010] respectively. The multiple-film method was used, and the intensities were estimated visually, taking into consideration both Cu $K\alpha$ and Cu $K\beta$ reflexions.

In Table 2 F values—both estimated and calculated —are listed. The f values of C and Cl used in the calculations are those of James & Brindley. No temperature factor was introduced.

The molecules have the shape indicated in Fig. 4; they do not possess other symmetry elements than the digonal axis demanded by the space group and ought to exhibit optical activity. The shape will not be altered by a conversion of the carbon ring, and a separation of *d* and *l* forms should therefore be possible in principle. Single crystals contain either *d* or *l* forms and must, in conformity with the crystal class D_2–222, be enantiomorphic. We have not been able to test this macroscopically; the small crystals used for the X-ray work had only a few faces developed, and larger crystals appeared to be twinned and gave the impression of possessing symmetry planes. This view was substantiated by the observation that the solution of a large crystal in dioxane did not show any optical activity. In the case of the tetrabromo-compound, of which good crystals are more easily obtained, small twinned crystals have been observed under the polarization microscope.

The 1ϵ, 2ϵ, 4κ, 5κ arrangement seems to be energetically very stable. 10 g. of the tetrachloro-compound were heated for 6 hr. to 230° C. with an excess of concentrated hydrochloric acid. After recrystallization of the product, about 80 % of the unchanged original compound melting at 174° C. were regained. The corresponding bromine compound is the chief product obtained when bromine is added to 1,4-cyclohexadiene. Owing to the lack of material we have not tried to prepare the chlorine compound in the corresponding way, but there seems to be little doubt that the tetrachlorocyclohexane of m.p. 174° C. will be formed in this reaction.

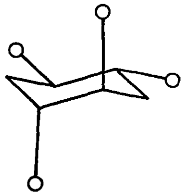

Fig. 4. Model of the $C_6H_8Cl_4$ molecule.

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Table 2. *Observed and calculated values of F_{hk0} and F_{h0l}*

(*hkl*)	$F_{\text{obs.}}$	$F_{\text{calc.}}$
200	10·4	10·3
400	19·9	17·5
600	0	2·4
110	10·0	9·4
210	4·3	5·9
310	17·3	11·5
410	5·7	7·6
510	5·2	− 6·8
610	3·5	6·7
710	3·9	6·0
020	0	2·5
120	3·5	4·7
220	29·4	−20·9
320	2·9	5·4
420	0	− 2·8
520	4·2	6·3
620	5·4	−10·6
720	2·1	4·0
130	11·7	−11·1
230	0	1·0
330	1·5	− 1·7
430	1·7	1·9
530	8·1	−12·6
630	2·3	− 2·6
730	4·2	3·0
040	11·3	14·1
140	2·1	2·4
240	3·6	− 3·6
340	2·1	− 0·9
440	8·0	10·7
540	0	− 0·3
640	0	2·8
740	0	− 4·0
150	2·3	4·9
250	0	1·4
350	6·3	12·1
450	3·8	4·7
550	0	1·9
650	1·7	1·1
750	3·9	14·1
060	0	2·0
160	2·6	3·5
260	6·6	−10·5
360	0	1·4
460	0	3·7
560	2·4	5·7
660	0	− 0·9
170	5·5	−12·9
270	0	− 1·5
370	2·1	− 5·0
470	0	1·4
570	3·5	−10·8
080	0	1·6
180	0	1·0
280	3·0	−10·0
380	2·8	− 6·5
001	1·6	− 1·8
101	0	− 0·8
201	25·8	21·0
301	0	− 0·4
401	1·1	1·0
501	3·4	− 7·0
601	2·6	7·9
701	0	− 1·8
801	0	4·2
901	1·3	− 6·5
002	22·6	12·4
102	11·6	−10·6
202	4·5	− 5·6
302	12·4	−13·6
402	3·9	4·9
502	0	− 2·1
602	1·1	− 2·4
702	3·7	−10·7
802	0	− 0·7
902	1·3	0·4
003	10·3	− 7·3
103	10·0	− 9·6
203	0	− 0·4
303	1·1	− 3·6
403	3·4	− 5·6
503	8·7	−15·6
603	0	− 1·9
703	0	− 2·2
803	0	− 2·2
903	2·6	−12·4
004	10·3	− 9·1
104	1·8	− 2·7
204	5·8	− 7·5
304	6·3	− 9·1
404	1·6	− 6·1
504	1·6	3·0
604	0·8	− 3·3
704	3·4	− 9·9
804	0	− 2·1
005	5·0	− 4·6
105	2·1	3·2
205	7·4	10·8
305	3·9	7·7
405	1·1	− 4·8
505	1·8	− 4·2
605	0·8	− 7·0
705	1·6	6·4
805	0	− 4·9
006	19·2	−16·8
106	5·3	7·9
206	2·6	− 4·2
306	1·1	2·9
406	3·4	− 9·8
506	2·4	9·0
606	0	− 0·9
706	0·8	− 1·1
007	1·6	5·5
107	1·3	3·3
207	3·7	− 7·7
307	1·6	6·3
407	0·8	3·7
507	0·8	3·7
008	0·8	− 2·8
108	2·1	5·8
208	4·5	10·8
308	1·8	5·4
408	0	0·2
508	0·8	4·4
009	4·7	11·9
109	0	1·6
209	0	0·4
309	0	0·8
409	2·4	9·7