

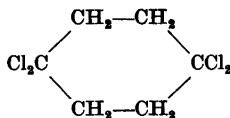
Crystal and Molecular Structure of 1,1,4,4-Tetrachlorocyclohexane

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A crystal structure determination of tetrachlorocyclohexane of m.p. 125° C led to a monoclinic unit cell containing 4 molecules with $a = 10.16$; $b = 7.73$; $c = 11.41$; $\beta = 91^\circ$. The space group is $C2/c$ and the molecules are centro-symmetrical. Fourier projections along b and c confirmed the structure formula corresponding to 1,1,4,4-tetrachlorocyclohexane which is in agreement with the first preparation of this compound from 1,4-cyclohexanedione and phosphorus pentachloride¹. The Cl—C—Cl angle is about 4° smaller than the "tetrahedral" angle. This is believed to result from the repulsion between the chlorine atoms and the nearest hydrogen neighbours. The angle between the (a) C—Cl bond and the chief axis of the carbon ring is 4° compared with the angle 7—8° found in the case of CHCl groups. The general features of the structure may be understood from an inspection of the b and c projections reproduced in Fig. 4a and 4b.

In the course of a series of structure determinations of tetrahalogeno-cyclohexanes which is being carried out in our laboratory we have investigated the structure of tetrachlorocyclohexane, m. p. 125° C, a substance first prepared by Kishner¹ more than sixty years ago from 1,4-cyclohexanedione and phosphorus pentachloride. The structure formula should therefore be



Besides testing the validity of this conclusion we hoped to be able to study the molecular structure in some detail. Parallel to the X-ray analysis an electron diffraction investigation was started which already in its earlier stages made it very probable that the structure formula given above is the correct one. A report of the electron diffraction investigation will be published shortly².

The substance used in both investigations was obtained by direct chlorination of cyclohexane in very much the same way as that described by Riem-schneider and Drescher³. Crystals were grown from ethyl ether and turned

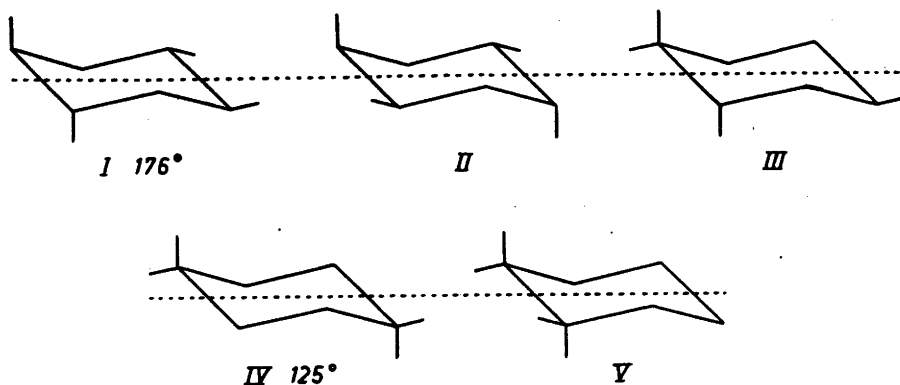


Fig. 1. Models of tetrachlorocyclohexanes all giving projections of the same kind along the dotted line. I : 1a,2a,4e,5e; II : 1a,2e,4a,5e; III : 1ae,2a,4e; IV 1ae,4ae; V 1ae,2ae.

out to be monoclinic. From Weissenberg and rotation photographs the following parameters of the unit cell were derived: $a = 10.16 \text{ \AA}$; $b = 7.73 \text{ \AA}$; $c = 11.41 \text{ \AA}$; $\beta = 91^\circ$. The space group is $C2/c$ and the density calculated assuming the unit cell to contain *four* molecules is 1.65 g/cm^3 which corresponds closely to the densities found for other tetrachlorocyclohexanes.

The Fourier projection of the molecule along the b -axis is shown in Fig. 2a; in Fig. 2b the projection obtained by Hassel and Wang Lund⁴ of the molecule

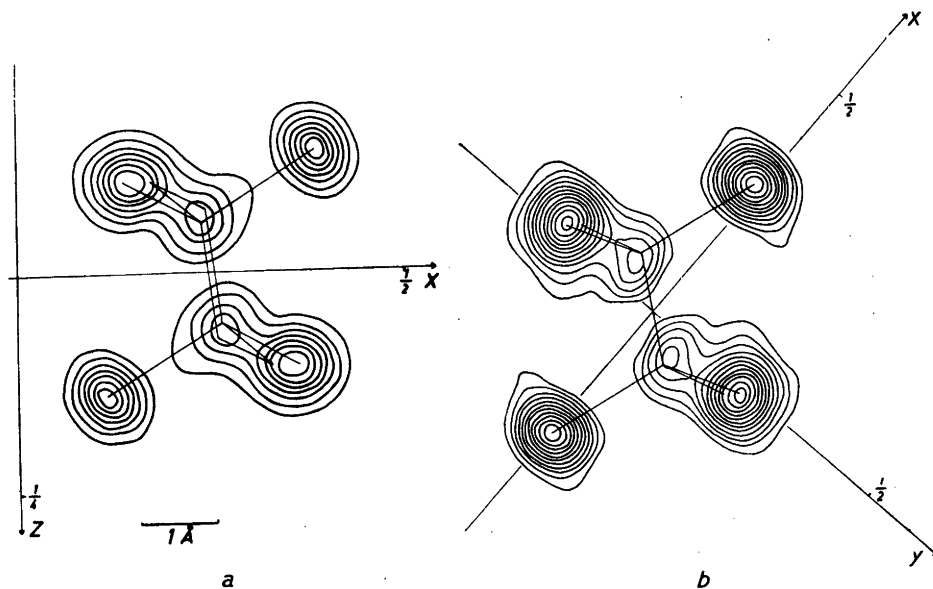


Fig. 2. a) Fourier projection of the 1ae, 4ae-tetrachlorocyclohexane molecule along the b -axis. b) corresponding projection of the 1a, 2a, 4e, 5e-tetrachlorocyclohexane molecule.

Table 1. Atomic coordinates of one molecule.

	<i>x</i>	<i>y</i>	<i>z</i>
Cl _{1a}	+ 0.112	+ 0.063	+ 0.139
(Cl _{4a})	+ 0.388	+ 0.437	- 0.139)
Cl _{1e}	+ 0.363	- 0.091	+ 0.110
(Cl _{4e})	+ 0.137	+ 0.591	- 0.110)
C ₁	+ 0.261	+ 0.079	+ 0.057
(C ₄)	+ 0.239	+ 0.421	- 0.057)
C ₂	+ 0.243	+ 0.095	- 0.075
(C ₅)	+ 0.257	+ 0.405	+ 0.075)
C ₃	+ 0.170	+ 0.255	- 0.108
(C ₆)	+ 0.330	+ 0.245	+ 0.108)

of 1a, 2a, 4e, 5e-tetrachlorocyclohexane * (m. p. 176° C) has been reproduced for comparison. The striking correspondence between the two projections does not, however, prove unambiguously that the substance is the 1,1,4,4-tetrachloro compound. All the molecules represented in Fig. 1 may of course give projections of the same kind. Among them there is even one, the 1a, 2e, 4a, 5e compound (II) which has a center of symmetry like the 1,1,4,4 compound (IV). The final proof for the correctness of the 1,1,4,4 structure was delivered by the working out of a Fourier projection along the *c*-axis (compare Fig. 3).

From the two refined Fourier maps all coordinate values for the chlorine atoms could be directly obtained. In the case of the *z* coordinate of the 1e chlorine atom, however, the accuracy may be somewhat inferior to the accuracy of the others because of overlapping with carbon atom 3 (6). For this carbon atom, on the other hand, the *x* and *y* coordinates could be determined with considerable accuracy. The other coordinates had to be evaluated under the assumption that the carbon ring is of the classical "chair" form with strictly tetrahedral valency angles. The C—C distances were assumed to be 1.54 Å, the C—Cl distances 1.78 Å. The coordinates are listed in Table 1. The number of observed reflexions, the intensity of which has been measured and used for the evaluation of the reliability factors were 52 for the *h* 0 *l* zone, 36 for the *h* *k* 0 zone, compared with the number of theoretically available reflexions (CuK-radiation) 77 and 58 respectively. The reliability factors thus obtained were 0.13 (*h* 0 *l*) and 0.14 (*h* *k* 0). The observed and computed structure factors are listed in Table 3.

Table 2.

	Ideal model	4° a-def. 1° e-def.	X-ray result
Cl _{1a} —Cl _{1e}	2.98	2.83	2.83
Cl _{1a} —Cl _{4a}	4.99	5.13	5.13
Cl _{1a} —Cl _{4e}	4.86	4.96	4.98
Cl _{1e} —Cl _{4e}	6.28	6.27	6.27

Computed Cl—Cl distances in an "ideal" and in a distorted model described in the text, both compared with directly observed distances.

* For the ϵ and κ bonds the new designations a (axial) and e (equatorial) suggested by Barton, Hassel, Pitzer and Prelog⁷ have been adopted.

Table 3. List of observed and computed structure factors.

<i>hkl</i>	<i>F</i> _{obs}	<i>F</i> _{calc}	<i>hkl</i>	<i>F</i> _{obs}	<i>F</i> _{calc}
002	7.7	+ 7.5	6010	3.3	+ 2.7
004	21.8	-23.0	6012	2.0	+ 2.2
006	5.3	- 4.0			
008	5.1	+ 6.3	802	4.7	+ 5.9
00 10	< 2.1	+ 0.1	804	5.7	- 5.5
00 12	1.8	- 2.0	806	4.1	- 4.5
00 14	< 1.3	0	808	< 2.0	+ 1.3
			8010	< 1.5	+ 1.0
200	10.6	-10.9			
400	13.9	-14.5	802̄	3.9	- 3.8
600	2.6	- 1.6	804̄	4.4	- 4.8
800	7.3	+ 7.8	806̄	4.0	+ 3.0
10 00	< 2.1	- 1.1	808̄	2.6	+ 1.9
12 00	< 1.6	- 0.9	8010̄	3.1	- 1.9
202	1.8	- 2.7	10 02	< 2.1	- 1.4
204	9.1	+ 9.1	10 04	< 2.0	+ 1.6
206	4.4	+ 3.3	10 06	1.6	+ 2.6
208	4.4	- 5.4	10 08	< 1.4	- 0.6
2010	< 2.1	- 0.5			
2012	2.6	+ 3.8	10 02̄	< 2.1	- 1.4
2014	< 1.2	+ 0.2	10 04̄	2.6	- 1.4
			10 06̄	< 1.8	+ 1.5
202̄	11.0	- 9.8	10 08̄	2.4	+ 1.7
204̄	7.3	- 6.6			
206̄	5.1	+ 4.9	12 02	2.0	- 2.2
208̄	9.1	+ 8.7	12 04	< 1.3	+ 0.7
2010̄	< 2.1	- 0.5			
2012̄	3.7	- 4.2	12 02̄	2.9	+ 3.1
2014̄	< 1.3	+ 0.1	12 04̄	1.3	+ 1.5
402	4.9	- 5.5	020	11.5	+14.1
404	10.8	+11.9	040	5.9	- 5.6
406	< 1.8	+ 1.7	060	11.9	-10.1
408	6.6	- 7.0	080	2.9	- 2.4
4010	2.0	- 2.1			
4012	1.6	+ 1.6	200	12.8	-11.0
			400	15.5	-15.0
402̄	12.0	+11.2	600	2.2	- 1.7
404̄	14.8	+15.2	800	7.5	+ 8.3
406̄	6.0	- 5.1	10 00	- 1.8	- 1.1
408̄	8.9	- 8.7	12 00	- 1.3	- 1.2
4010̄	< 2.1	+ 0.2			
4012̄	1.6	+ 2.0	110	1.8	+ 2.1
			130	3.2	+ 3.5
602	< 1.7	+ 0.3	150	2.4	+ 2.0
604	2.4	- 3.2	170	- 1.8	- 1.0
606	< 2.0	- 0.8	190	1.8	- 2.0
608	4.4	+ 5.2			
6010	1.8	+ 2.3	220	1.6	- 0.7
6012	1.8	- 2.5	240	1.8	+ 1.8
			260	2.9	+ 2.8
602̄	3.3	- 1.4	280	- 1.6	- 0.4
604̄	2.4	+ 1.8			
606̄	< 2.0	- 1.5	310	2.7	+ 3.2
608̄	2.9	- 2.1	330	2.7	- 2.7

<i>hkl</i>	F_{obs}	F_{calc}	<i>hkl</i>	F_{obs}	F_{calc}
350	4.5	- 3.3	750	3.3	+ 2.9
370	- 1.8	- 0.6	770	- 1.6	+ 0.0
390	1.6	+ 1.7			
			820	5.1	+ 5.5
420	5.9	- 6.3	840	3.8	- 3.4
440	- 1.6	+ 1.8	860	3.6	- 4.1
460	4.9	+ 5.3			
480	1.8	+ 2.1	910	3.7	+ 3.1
			930	- 1.8	+ 1.2
510	4.0	- 4.4	950	- 1.6	- 0.6
530	- 1.6	- 2.6	970	- 0.9	- 1.4
550	- 1.8	- 0.1			
570	- 1.8	+ 2.0	10 20	- 1.8	+ 0.3
590	0.9	+ 1.7	10 40	- 1.6	+ 1.5
			10 60	- 0.9	+ 1.0
620	3.8	- 3.7			
640	- 1.8	+ 1.0	11 10	2.5	+ 2.6
660	- 1.8	+ 0.7	11 30	- 1.6	- 0.1
680	2.0	+ 1.6	11 50	1.8	- 1.8
710	2.5	- 3.3	12 20	2.0	- 1.4
730	- 1.8	+ 1.3	13 10	1.6	- 1.7

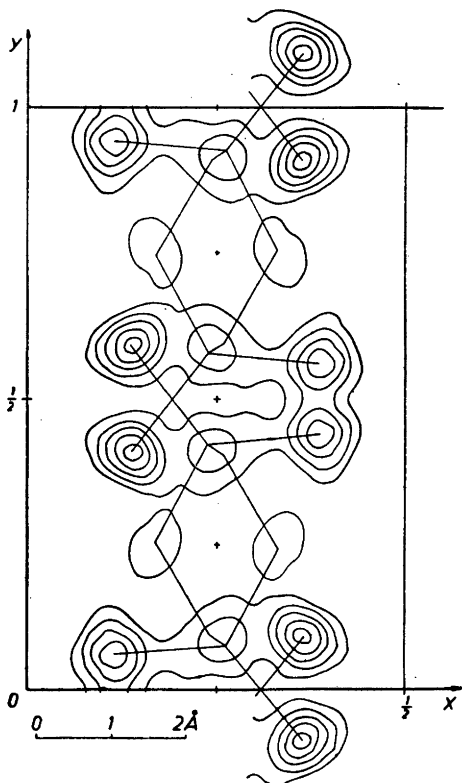


Fig. 3. Fourier projection of the 1ae, 4ae-tetrachlorocyclohexane molecule along the *c*-axis.

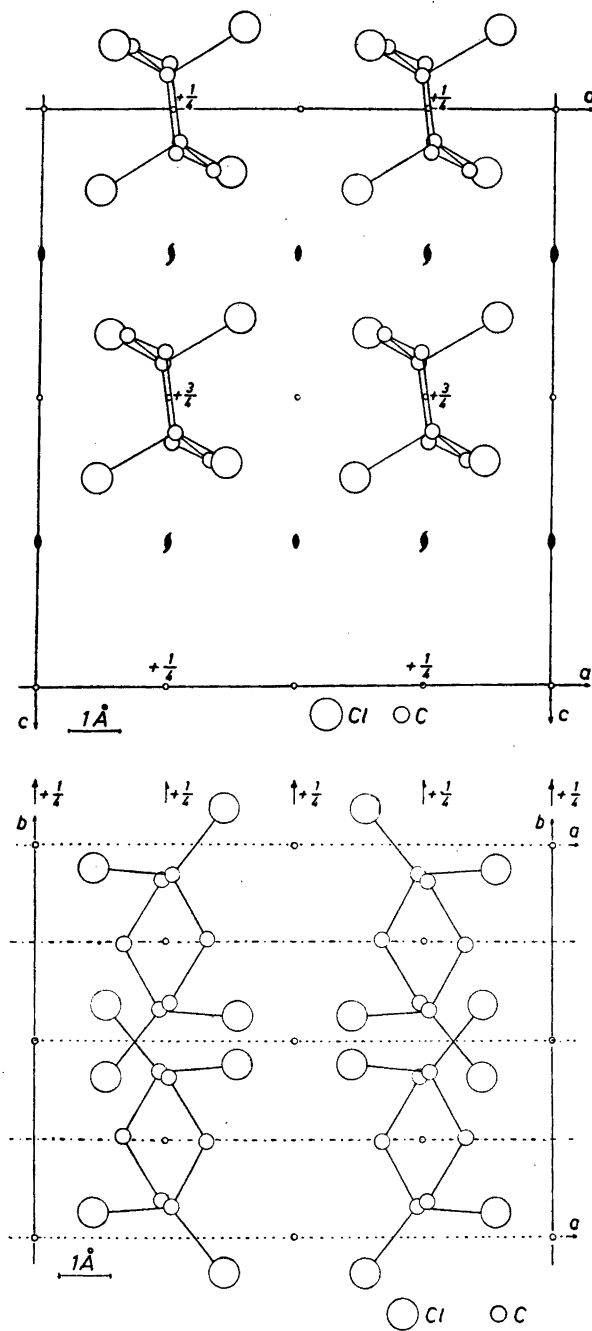


Fig. 4. Projections of the structure, a) along the b-axis, b) along the c-axis.

The assumed C—Cl distance of 1.78 Å is about one hundredth of an Ångström shorter than the mean value found in previous structure determination of chlorinated *cyclohexanes* in which *one* chlorine atom only is attached to each carbon atom. A certain shortening of the bond in CCl_2 groups appears reasonable. In the case of methylene chloride the microwave spectroscopical value ⁵ is 1.7724 ± 0.0005 Å, approximately half way between the bond length in carbon tetrachloride and methyl chloride. In the present structure determination the value derived for the Cl—C—Cl angle will depend to some extent on the length attributed to the C—Cl bond. With the value 1.78 Å the angle becomes 105.3° , should it be one hundredth of an Ångström shorter the angle would become 106.1° . It therefore appears rather certain that the angle is in fact somewhat smaller than the "tetrahedral" angle. The explanation of this "compression" of the angle may, we think, be found in the repulsion exerted on the two chlorine atoms by the nearest (a) hydrogen atoms of the same molecule. In the case of Cl_{1a} the repelling hydrogen atoms would be the 3a and 5a atoms, and for the other chlorine atom (Cl_{1c}) the hydrogen atoms 2a and 6a. Such a view appears to be strengthened by the fact that the best agreement between observed and calculated Cl—Cl distances is obtained by assuming that the chlorine atoms all remain in the plane containing the carbon atoms 1 and 4 and the chief axis of the carbon ring. The angle between the C_1 — Cl_{1a} direction and this axis thus becomes 4° (compared with 7 or 8° previously found in CHCl groups ^{4,6}) and the acute angle between the chief axis and the C_1 — Cl_{1c} bond 1° smaller than it would be in an undistorted structure. It may be added that the distortions from an "ideal" structure just described are in good agreement with the results obtained in the course of the electron diffraction investigation ². The extent of agreement obtained between observed and computed Cl—Cl distances on the basis of the model just described may be judged from Table 2. That the bending angle of the (a) C—Cl bond away from the trigonal axis is smaller for CCl_2 groups than for CHCl groups appears rather natural as stated above, when the distance between the (e) chlorine atom and its nearest hydrogen neighbours is also being considered.

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