

The Transition Occurring in Solid *trans*-1,4-Dichlorocyclohexane at 12°C

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An investigation of the transition taking place in solid *trans*-1,4-dichlorocyclohexane at 12°C has brought out that the monoclinic low-temperature form is transformed into a tetragonal form having the lattice constants:

$$a = 6.82 \text{ \AA}; c = 8.55 \text{ \AA}$$

and a density of 1.25 g/cm³. The unit cell therefore contains *two* molecules. The space group is $P4_2/mnm$. Due to extraordinary strong thermal damping the number of independent X-ray reflexions measured even in a three-dimensional investigation is very limited. It could be stated, however, that the conformation of the molecule is *diequatorial* as it is also in the low-temperature form. The structure is a disordered one, but the position of the chlorine atoms is fairly well defined because they are situated not far from the axis of "rotation". The transition of *mixed* crystals containing also the corresponding dibromo-compound has been studied.

The fact that the carbon ring in simple cyclohexane derivatives is almost always present in the "chair" form leaves two main possibilities for the configuration of *trans*-1,4-derivatives, the diaxial (*aa*) and the diequatorial (*ee*) conformations. In the crystalline bromine and iodine derivatives and in the modification of the chlorine derivative stable below 12°C the molecule is present in the *ee* conformation. Crystals of the chlorine derivative, unlike those of the bromine or iodine derivatives, has a transition point (at 12°C),¹ however, and it was not known if this transition is connected with a conformational change of the molecule. Such a connection appeared possible particularly because electron diffraction measurements have shown that the two conformations are present in nearly equal proportions in the vapour.²

A striking feature of the crystals is their high vapour pressure at room temperature and the X-ray investigation at once revealed a pronounced thermal damping resulting in a very limited number of reflexions in the diagrams.

Crystals were obtained by slow sublimation at room temperature. The X-ray investigation showed that they are tetragonal with lattice constants:

$a = 6.82 \text{ \AA}$; $c = 8.55 \text{ \AA}$. The macroscopic density was found equal to 1.25 g/cm^3 and the number of molecules in the cell is therefore $Z = 2$.

Stationary crystal diagrams showed the Laue symmetry to be $4/mmm$. The two-dimensional intensity material was collected partly with an integrating Weissenberg camera (the $0kl$ -zone) and partly with a precession camera ($hk0$ - and $h0l$ -zones) using one and the same crystal. Weissenberg diagrams were taken with $\text{CuK}\alpha$ -radiation, precession diagrams with $\text{MoK}\alpha$ -radiation.

The three-dimensional material was obtained from integrated equi-inclination Weissenberg diagrams from a crystal oscillating about the a -axis and using $\text{MoK}\alpha$ -radiation. Tin foil was inserted as an absorbing material between the films and the longest exposure time for a particular layer was 125 h. The total number of independent reflexions observed was 69. The intensities of sufficiently strong reflexions were measured photometrically, the intensities of the weakest reflexions were estimated visually. The number of equivalent reflexions repeated in different layers was sufficiently large to permit the evaluation of interlayer scale factors.

The determination of the structure based on the two-dimensional material and assuming the space group to be $Pnmm$ did not lead to acceptable results. Including the three-dimensional data we now based our further work on the assumption that the true space group is $P4_2/mmm$. If the structure were an ordered one this would mean that we imposed symmetry requirements on the molecule which would not be acceptable from a chemical point of view. But there are indeed so strong indications of the structure being disordered that this objection did not appear very serious. An NMR investigation of the crystals at temperatures below and above that transition point (at 5° and 15°C) actually showed that some kind of "rotational" motion of the molecule is present at the higher temperature that does not persist below the transition point.

It was expected that the "rotation" would take place about a fixed axis and that the distance of the heaviest (chlorine) atoms from this axis is comparatively small. Ordinary and sharpened Patterson sections could actually be interpreted by assuming the axis of "rotation" to run along the diagonal $[110]$ and that one of the chlorine atoms belonging to a molecule having its centre of symmetry at the origin has the approximate coordinates $(0.325, 0.325, 0)$. This would mean that the intramolecular Cl—Cl distance is about 6.3 \AA and that the molecule is present in the diequatorial conformation. This assumption made it possible to interpret even some of the lower peaks as being caused by carbon-chlorine distances.

From previous investigations the structures of the diequatorial form of the free molecule is fairly well known.² The interatomic distances and angles employed are listed in Table 1.

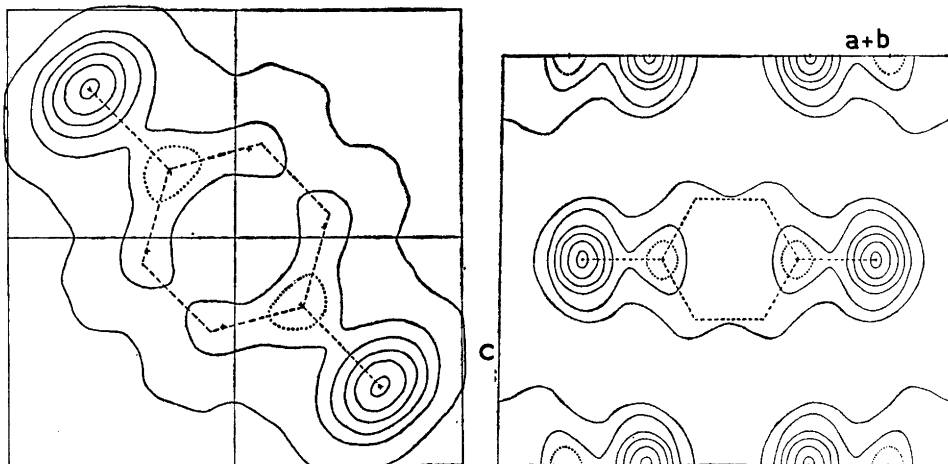
A single "resting" position together with the equivalent position obtained by a rotation of 180° about the $[110]$ direction (set A) was first considered.

Table 1. Interatomic distances and angles in the *trans*-1,4-dichlorocyclohexane model.²

Distances		Angles	
C—H	1.10 \AA	CCC	111.5°
C—C	1.53 \AA	CCH	108.6°
C—Cl	1.81 \AA	CCCl	108.6°
		ClCH	111.5°

The distance of one Cl atom from the plane $z = 0$ was assumed to be $0.06 c$. With the particular model of the molecule we have chosen, *two* different atomic arrangements are possible, however. A majority of the structure factor signs turned out to be the same in both cases and a three-dimensional Fourier synthesis was therefore performed including all such reflections if they had appreciable F_{obs} -values. From the resulting map a decision between the two possibilities was possible. A close inspection of the Fourier map indicated, however, that a second set of "resting" positions (B) should also be considered, those obtained from (A) by a rotation of 90° , about the axis. Retaining our molecular model it became possible to evaluate the ratio of the weight factors of (A) and (B). The (isotropic) damping factor B was put equal to 9.5 for all atoms. The ratio of the weight factors thus computed was 0.56:0.44 and the final R value of the structure was 0.186.

In Figs. 1 and 2 the final Fourier sections (001) and (110) are reproduced. Observed and calculated structure factors are listed in Table 2.



Figs. 1 and 2. Fourier sections (001) and (110). Contours at intervals of $0.5 \text{ electrons}/\text{\AA}^3$.

Intermolecular distances between atoms appear to be in good agreement with those to be expected. Distances between chlorine atoms are fairly well defined and lie between 3.4 and 3.6 \AA .

It may appear somewhat surprising that two substances so similar as the *trans*-1,4-dichloro and dibromocyclohexane which are isomorphous at temperatures below 12°C behave so differently at higher temperatures. There is indeed no indication of a transition taking place in the bromine compound.

We have carried out some experiments with mixed crystals containing the chlorine and bromine compound. Monoclinic single crystals were obtained from methanol solutions, the density of each crystal determined employing the flotation method and the transition temperature measured using a polar-

Table 2. Observed and calculated structure factors.

h	k	l	$ F_o $	$ F_c $	h	k	l	$ F_o $	$ F_c $
0	0	2	35.8	35.8	1	5	0	1.4	— 1.3
0	0	4	4.8	9.2	1	5	1	1.8	2.5
0	0	6	< 1.1	2.9	1	5	2	1.2	1.3
0	1	1	7.8	7.1	1	5	3	1.1	1.3
0	1	3	5.2	— 3.4	1	5	4	< 0.9	0.5
0	1	5	2.2	— 1.3	1	5	5	1.1	0.2
0	1	7	< 1.2	1.2	2	2	0	3.9	0.3
0	2	0	11.4	— 11.4	2	2	1	6.8	— 9.6
0	2	2	9.0	— 10.0	2	2	2	0.6	— 0.9
0	2	4	3.7	— 3.6	2	2	3	3.1	— 2.4
0	2	6	< 1.1	0.3	2	2	4	1.0	— 1.4
0	3	1	5.8	5.6	2	2	5	< 1.1	— 0.3
0	3	3	3.5	1.3	2	2	6	< 1.2	— 0.8
0	3	5	1.1	1.1	2	3	0	4.4	— 5.5
0	4	0	1.9	— 2.9	2	3	1	6.6	— 5.3
0	4	2	1.8	— 1.4	2	3	2	2.4	— 2.2
0	4	4	0.8	— 0.4	2	3	3	2.3	— 2.0
0	5	1	0.9	1.3	2	3	4	< 1.0	— 0.7
0	5	3	0.8	0.4	2	3	5	< 1.1	— 0.1
0	6	0	1.2	— 0.7	2	3	6	< 1.2	— 0.6
0	6	2	0.8	— 0.6	2	4	0	1.5	2.2
1	1	0	14.6	16.3	2	4	1	3.0	3.2
1	1	1	18.2	— 20.3	2	4	2	1.7	2.1
1	1	2	4.3	— 3.8	2	4	3	2.0	2.1
1	1	3	7.8	— 7.8	2	4	4	1.1	1.1
1	1	4	< 0.9	— 0.1	2	4	5	< 1.1	0.0
1	1	5	2.0	1.3	2	5	0	< 0.7	0.9
1	1	6	< 1.1	0.8	2	5	1	0.8	— 0.6
1	1	7	< 1.2	0.1	2	5	2	< 0.8	0.8
1	2	0	9.1	8.7	2	5	3	0.8	— 0.3
1	2	1	2.6	3.1	3	3	0	3.0	5.0
1	2	2	7.1	7.3	3	3	1	1.1	0.1
1	2	3	1.1	0.4	3	3	2	3.4	3.5
1	2	4	2.6	1.5	3	3	3	1.2	1.8
1	2	5	< 1.0	— 0.1	3	3	4	2.5	0.8
1	2	6	< 1.1	— 0.7	3	3	5	< 1.2	0.7
1	3	0	7.0	— 7.1	3	4	0	0.9	— 1.2
1	3	1	0.7	— 0.9	3	4	1	< 0.9	0.5
1	3	2	4.4	— 4.5	3	4	2	< 0.9	— 0.3
1	3	3	0.9	1.0	3	4	3	< 1.0	0.8
1	3	4	1.2	— 1.5	3	4	4	< 1.1	— 0.1
1	3	5	< 1.0	— 0.2	3	5	0	0.9	— 1.1
1	3	6	< 1.1	0.0	3	5	1	< 0.9	— 1.1
1	4	0	2.7	— 2.8	3	5	2	< 1.0	— 0.5
1	4	1	0.9	— 1.2	4	4	0	1.0	— 0.8
1	4	2	2.1	1.0	4	4	1	1.7	— 2.5
1	4	3	< 0.8	— 0.6	4	4	2	< 1.1	— 0.6
1	4	4	0.7	0.8	4	5	0	1.1	— 0.2
1	4	5	< 1.1	— 0.6	4	5	1	1.1	0.6

izing microscope. The composition of each individual crystal was determined by assuming that the density varies linearly with the mole fraction. It was found that a continuous unbroken series of mixed crystals is actually formed and the curve giving the transition temperature as a function of the mole fraction was found to be at least nearly linear. The curve is actually so steep that the extrapolated transition temperature for the pure bromine compound (145°) lies well above the melting point (112°C). It may be added that the *trans*-1,4-chlorobromocyclohexane does not undergo a transition although it has a structure corresponding to that of the other *trans* di-substituted 1,4-compounds at room temperature.¹

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