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Molecular Configuration of 1,2-Dichloro-4,5-dibromocyclohexane ($\varepsilon, \varepsilon-\varkappa, \varkappa \rightleftharpoons \varkappa, \varkappa-\varepsilon, \varepsilon$) in the Crystal

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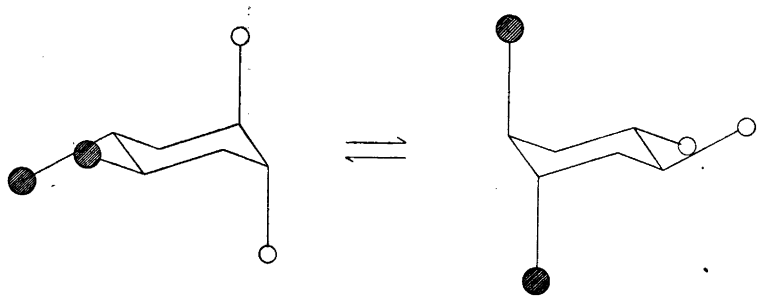
Recently Hassel and Lunde [1] prepared a new member of the series of 1,2,4,5-tetrahalogeno-cyclohexanes (1,2-dichloro-4,5-dibromocyclohexane, m.p. 171° C) from 1,2-dichlorocyclohexene and bromine. They expected to obtain a substance corresponding to the tetrachloro- and tetrabromocyclohexanes melting at 176° C and 187° C respectively, the structure of which has been determined [2,3] and corresponds to the configuration 1ε, 2ε, $4\varkappa$, $5\varkappa$.

We actually found the crystals of the new substance to be isomorphous with those of the two tetrahalogeno-compounds just mentioned. In Table 1 the lattice constants are listed. The number of molecules in the unit cells is 2, the space group is $P2_1\,2_1\,2$ and the molecules therefore have a two-fold axis of symmetry.

Table 1. Lattice constants of the three tetrahalogeno-compounds in Å.

	a	*b*	*c*
$C_6H_8Cl_4$	7.60	7.54	7.72
$C_6H_8Br_4$	7.90	7.98	7.89
$C_6H_8Cl_2Br_2$	7.69	7.67	7.83

A more detailed analysis of the structure was subsequently carried out in order to decide whether the structure is of a disordered type, the chlorine and bromine atoms occupying ε and $\varkappa$ positions in a statistical way, or if all the molecules have the same configuration. In the latter case it seemed of interest to determine which of the two interconvertible forms is present in the crystal, the form (Fig. 1a) having the chlorine atoms in ε positions or the form (Fig. 1b) in which the chlorine atoms are in $\varkappa$ positions. A priori it would seem most probable that the chlorine atoms are in ε position because the repulsion



Figs. 1 a and b. Possible configurations of the 1,2-dichloro-4,5-dibromocyclohexane (ε, $\varepsilon-\varkappa$, $\varkappa$).

between a halogen atom in ε position and the two nearest hydrogen atoms, also in ε positions, would be expected to raise the energy of the molecule more if it is a bromine atom than if it is a chlorine atom. The repulsion effect of two halogen atoms in neighbouring $\varkappa$ positions would probably be less important to the energy of the molecule.

It was a great advantage to our investigation that the structure of the tetrachloro-compound was already known in some detail. In the case of the tetrabromo-compound the parameters of the bromine atoms had also been determined, but the positions of the carbon atoms were rather uncertain. K. Taugböl of our laboratory therefore worked out a Fourier projection of the bromine compound which settled with certainty that the parameters of all corresponding atoms have nearly identical values in the tetrachloro- and the tetrabromo-compounds.

Rotation and Weissenberg photographs obtained from the new compound were so similar to those of the compounds containing only chlorine or bromine that it must be assumed that the halogen atoms have nearly the same parameters in the three cases. In order to work out a Fourier projection along the c axis in which the halogen atoms would be well separated, intensity values of ($hk0$) reflexions were determined from Weissenberg photographs with rotation about [001]. The exposure times of the double films were 1, 5 and 20 hours respectively. The intensities of both CuK_α and K_β reflexions were considered. A standard scale was prepared using a strong reflexion from the crystal itself as a source of radiation.

As the first structure alternative, a statistical distribution of halogen atoms over ε and $\varkappa$ positions did not give a satisfactory agreement between observed and calculated intensities of ($hk0$) reflexions, we calculated the inten-

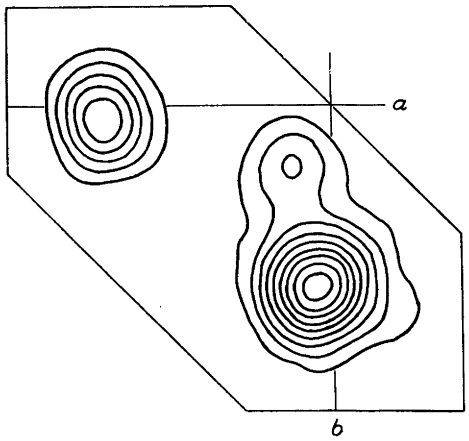


Fig. 2 a. Projection of the electron density of dichloro-dibromocyclohexane along the c axis.

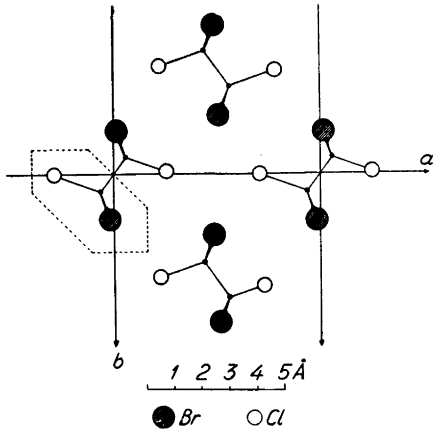


Fig. 2 b. The structure of dichloro-dibromocyclohexane projected along the c axis.

sities assuming the chlorine atoms to be in ε positions, the bromine atoms in $\varkappa$ positions (Fig. 1a) and obtained a very satisfactory agreement with observed intensities. The resulting electron-density map showed a marked difference in the heights of the ε and $\varkappa$ halogen peaks. The x and y parameters thus obtained differed very little from those first assumed, and a single amplitude only changed its sign.

The refined Fourier map is reproduced in Fig. 2a. Neighbouring contour lines correspond to a drop in electron density equal to 5 electrons per square Ångström. Comparing Fig. 2a with Fig. 2b which gives a full projection of the structure along the c axis (the area whithin the dotted hexagon corresponds to the Fourier map of Fig. 2a) it is easily seen that the chlorine atoms are situated in ε positions, the bromine atoms in $\varkappa$ positions.

The presence of two of the carbon atoms is indicated by a smaller peak extending from the peak due to the ($\varkappa$) bromine atom. In the case of an undeformed carbon ring (with strictly tetrahedral valency angles) the projections of these two carbon atoms would coincide. The projection of the third, crystallographically independent, carbon atom nearly coincides with that of the bromine atom and thus contributes to the height of the bromine peak. Taking this contribution into account, the relative heights of the two halogen peaks are in good agreement with the ratio to be expected.

The aim of the crystal structure investigation was to determine the configuration of the molecules and not the exact parameters of the atoms. It is possible, however, from the Fourier projection along [001] to obtain fairly accurate x and y values for the halogen atoms (compare Table 2).

Table 2. x and y parameters of the dichloro-dibromo-compound.

	x	y
Cl	− 0.282	0.020
Br	− 0.019	0.222
C_1,C_5	− 0.062	0.081
C_6	− 0.028	0.194

Table 3. Observed and calculated $|F|$ values of (hkO) reflexions.

*hk*0	F_{obs}	F_{calc}	*hk*0	F_{obs}	F_{calc}
200	22.3	23.9	440	10.5	9.4
400	23.5	21.0	540	0	1.4
600	2.8	4.4	640	2.3	2.7
800	0	1.5	740	0	2.2
110	11.5	11.7	840	0	1.4
210	7.4	9.1	150	5.0	7.9
310	13.8	10.9	250	1.6	1.4
410	9.9	10.6	350	8.4	9.0
510	5.0	2.9	450	4.4	4.2
610	6.0	6.4	550	0	2.9
710	3.2	2.3	650	1.8	1.1
810	3.9	3.7	750	3.9	3.3
910	2.9	1.3	850	2.2	1.5
020	9.1	12.3	060	2.5	2.5
120	4.9	6.4	160	3.1	3.5
220	35.4	30.0	260	8.5	6.6
320	3.5	4.7	360	0	1.0
420	5.5	9.0	460	0	0.8
520	4.4	5.0	560	3.1	3.3
620	6.8	7.5	660	0	1.0
720	2.3	2.0	760	0	1.7
820	2.4	2.4	170	6.5	7.4
920	0	1.0	270	0	1.2
130	13.9	14.2	370	2.9	4.0
230	2.1	2.5	470	0	0.3
330	3.2	5.3	570	3.5	3.2
430	0	1.5	670	1.6	1.1
530	8.0	6.7	080	0	0.5
630	3.8	4.1	180	0	0.6
730	2.6	0.1	280	0	1.1
830	1.6	1.9	380	2.5	2.5
930	1.4	1.3	480	0	0.6
040	21.1	17.6	580	0	1.1
140	2.8	2.6	190	0	2.2
240	2.5	5.5	290	0	0.6
340	2.9	3.4	390	1.4	2.1

As regards the carbon atoms, parameter values obtained from the structure analysis of the tetrachloro-compound were used, when calculating F values (compare Table 2). A temperature factor $e^{-5,15\left(\frac{\sin\vartheta}{\lambda}\right)^2}$ was introduced.

It is worth mentioning that the good agreement obtained between calculated and observed $|F|$ values (compare Table 3) would not have been reached if the influence of the carbon atoms had been disregarded. The low value of the reliability factor (0.20) seems indeed to justify the choice of the carbon parameters mentioned above.

The final result of our investigation thus confirms the anticipation concerning the relative stability of the two possible configurations of the molecule. It should be borne in mind, however, that the molecules are not "free" and that the effect of intermolecular forces has not been considered. Although we think it very probable that the configuration found in the crystal will be that which predominates in the vapour, it would indeed seem worth while to determine the configuration in the vapour phase also, using electron diffraction technique. Such investigations have already been started in our laboratory, but experimental difficulties due to thermal instability of the dichloro-dibromo-compound have prevented us from giving final results in the present communication.

SUMMARY

A new substance, 1,2-dichloro-4,5-dibromo-cyclohexane [1], isomorphous with the tetrachloro- and tetrabromocyclohexanes in which the halogen atoms occupy 1ε, 2ε, $4\varkappa$, $5\varkappa$ positions, has been studied in the solid state. It was found that the chlorine atoms are in ε positions, the bromine atoms in $\varkappa$ positions. It seems probable that this configuration corresponds to a lower energy of the molecule than the configuration in which the chlorine atoms occupy $\varkappa$ positions, the bromine atoms ε positions even in the gasous state.

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