1e,2e-Dichloro-4e,5e-dibromocyclohexane, a Disordered Crystal Structure

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The crystal structure of one modification of 1e,2e-dichloro-4e,5e-dibromocyclohexane has been determined. The space group requires the molecule to possess a center of symmetry which is incompatible with chemical evidence. The structure is therefore assumed to be disordered and Fourier projections support this assumption.

In a previous publication Hassel, Wang Lund and Lunde¹ reported the preparation of several 1,2,4,5-tetrahalogenocyclohexanes. The addition of bromine to 1,2-dichlorocyclohexene(4) led to two different 1,2-dichloro-4,5-dibromocyclohexanes, one melting at 171° C, the other at 240° C. The structure of the former has been settled by X-ray² and electron diffraction³ methods to be 1a,2a-dichloro-4e,5e-dibromocyclohexane⁴. The compound melting at 240° C was shown to be dimorphous with an α -modification stable below 90—95° C and a β -modification stable at higher temperature. Corresponding phases α and β have been shown to exist both for the corresponding tetrachloro- and the tetrabromocompound. Further, the crystals of the α -modifications of the three compounds have been found isomorphous, as well as those of the β -modifications^{1,5}. Both structures are monoclinic with somewhat different crystallographic data.

From the fact that both modifications crystallize in the monoclinic space group $P2_1/c$ with two molecules in the unit cell, it follows that the center of the molecule has to lie in the twofold position which requires a center of symmetry. This fits well into the picture of a molecular structure with all four substituents in equatorial positions in those cases where the halogens are all of the same kind. In the case of a mixed compound of the type 1,2-dichloro-4,5-dibromocyclohexane it must however be concluded that the structure is of a disordered type in such a manner that the average symmetry corresponds to that of a center.

This kind of disorder has been found by Hendriks for *p*-chloro-bromobenzene⁷, and a more recent demonstration has been given by Hassel and Hadler Vihovde⁸ in the crystal structure of *trans* 1,4-chloro-bromocyclohexane.

Fig. 1. Fourier projection along $[010]$.

Fig. 2. Fourier projection along $[100]$.

As rather few cases of such displacement disorder are known in structures of organic compounds it was found worth while to study in more detail one of the disordered modifications of the compound in question.

The structure of the β -modification of the tetrabromocompound has been worked out earlier by Haak⁶. The α -modifications represent however a new type of structure, therefore this was chosen for detailed study. To repeat, the crystallographic data are: $a = 6.29$ Å, $b = 6.93$ Å, $c = 10.81$ Å, $\beta = 98^\circ$. Weissenberg equator diagrams of the zones $(h0l)$ and $(0kl)$ were taken with Cu— $K\alpha$ radiation using the multiple film technique. Three double sets of films were given exposure times in the ratio 20/5/1. Heavily exposed films did not give any signs of reflexions not compatible with the space group $P2_1/c$. For the estimation of intensities a standard scale was prepared using one of the stronger reflexions from the very same crystal used when taking the diagrams.

In the calculation of theoretical structure factors a common atomic scattering factor for all halogen atoms was taken to be the arithmetic mean of the f -values for chlorine and bromine, given by the Hartree and Thomas-Fermi f -curves respectively.

Trial and error analysis taking into account only the strongest reflexions soon gave a reasonable agreement between observed and calculated structure factors. Further refinement gave as result the Fourier maps reproduced in Figs. 1 and 2. In these the interval between contour lines corresponds to 3 electrons/Å² starting at 3 electrons/Å². The halogen parameters obtained from the maps are given in Table 1. The presence of the carbon atoms gives rise to clearly separated peaks, but only approximate coordinates can be given. The x and z values listed in Table 1 are determined from the (010) projection,

Table 2. Observed and calculated structure factors.

<i>hkl</i>	$ F_{\text{obs}} $	$ F_{\text{calc}} $	<i>hkl</i>	$ F_{\text{obs}} $	$ F_{\text{calc}} $
100	1.9	3.5	50 $\bar{8}$	0	1.0
200	26.1	26.8	60 $\bar{8}$	5.7	4.3
300	21.2	20.6	10 $\bar{1}0$	4.7	4.3
400	3.2	6.3	20 $\bar{1}0$	6.2	6.7
500	9.5	10.9	30 $\bar{1}0$	5.4	4.5
600	0	2.3	40 $\bar{1}0$	0	0.5
700	0	3.2	50 $\bar{1}0$	5.0	4.0
002	0	3.0	011	6.7	4.0
102	32.4	34.9	012	6.0	8.1
202	3.0	3.6	013	6.7	6.5
302	10.6	11.8	014	16.6	17.2
402	7.8	9.0	015	12.9	13.7
502	3.1	3.3	016	10.3	10.4
602	0	3.8	017	3.8	3.0
004	0	2.2	018	0	1.5
104	0	0.7	019	3.1	2.7
204	0	0.6	0110	3.5	3.1
304	0	1.2	020	11.3	9.7
404	0	0.5	021	31.5	27.1
504	0	0.3	022	7.0	6.0
604	0	0.3	023	0	1.7
006	10.0	11.0	024	3.5	4.3
106	9.0	8.6	025	6.3	6.3
206	0	2.2	026	4.1	5.7
306	8.2	10.6	027	4.3	4.5
406	0	0	028	0	1.7
506	0	3.4	029	6.7	6.2
008	2.1	2.0	031	8.2	8.0
108	8.5	10.3	032	5.8	7.2
208	6.4	6.9	033	0	0.7
308	0	2.1	034	6.4	6.2
408	5.1	6.6	035	16.1	15.3
0010	6.2	6.1	036	3.4	3.7
1010	0	0.5	037	0	0.9
2010	4.3	4.2	038	5.6	5.2
10 $\bar{2}$	23.5	23.2	040	15.6	13.0
20 $\bar{2}$	23.2	19.9	041	5.0	4.4
30 $\bar{2}$	0	4.5	042	6.6	6.6
40 $\bar{2}$	13.6	14.2	043	9.6	9.8
50 $\bar{2}$	6.4	4.6	044	4.7	5.0
60 $\bar{2}$	4.7	5.9	045	0	2.9
10 $\bar{4}$	0	1.8	046	0	1.4
20 $\bar{4}$	5.1	0.9	047	0	2.8
30 $\bar{4}$	4.7	4.6	048	0	1.3
40 $\bar{4}$	5.3	3.0	051	4.6	5.6
50 $\bar{4}$	2.2	4.2	052	3.3	2.8
60 $\bar{4}$	0	0.8	053	2.4	3.4
10 $\bar{6}$	5.4	3.3	054	4.9	5.4
20 $\bar{6}$	10.7	9.8	055	0	1.0
30 $\bar{6}$	1.9	2.6	056	4.3	3.8
40 $\bar{6}$	4.8	3.0	057	3.5	4.0
50 $\bar{6}$	5.2	4.4	060	5.1	4.1
60 $\bar{6}$	0	0.7	061	3.1	2.9
10 $\bar{8}$	13.3	12.9	062	2.5	2.3
20 $\bar{8}$	6.2	6.7	063	4.3	6.0
30 $\bar{8}$	8.1	8.2	064	0	3.2
40 $\bar{8}$	7.7	6.9	065	0	0.5

Fig. 3. Projection of the structure of α -1e,2e,4e,5e-tetrahalogeno cyclohexane on (010).

the y values from the (100) projection. In Figs. 3 and 4 are reproduced projections of the structure on (010) and (100).

In order to normalize calculated structure factors and to determine an appropriate temperature factor the ratio of observed to calculated structure factors was plotted as a function of $\sin \theta$. To this set of points a curve of the

Fig. 4. Projection of the structure of α -1e,2e,4e,5e-tetrahalogeno cyclohexane on (100).

Table 1. Parameters of halogen and carbon atoms.

	<i>x</i>	<i>y</i>	<i>z</i>
Hal ₁	-0.305	0.322	0.094
Hal ₂	-0.294	-0.121	0.211
C ₁	-0.195	0.138	0.021
C ₂	0.088	0.050	0.111
C ₃	0.003	-0.178	0.054

form $k \exp(-a \sin^2 \theta)$ was adjusted by inspection. For both projections the constant a was found equal to 2.16. After normalizing calculated structure factors and taking the temperature factor into account the agreement factor $\Sigma ||F_{\text{obs}}| - |F_{\text{calc}}|| / \Sigma |F_{\text{obs}}|$ was calculated to be 0.18 and 0.17 for the two projections (010) and (100) respectively. In Table 2 observed and calculated F -values are listed.

From the Fourier maps it will be seen that the two crystallographically nonequivalent halogen peaks are of about the same height. Rough calculations give a total number of 25 electrons associated with both peaks. Although such a number cannot be expected to be too reliable it is of interest to compare these features of the structure with the situation in the structure of 1a,2a-dichloro-4e,5e-dibromocyclohexane of m.p. 171° C. There the crystallographically nonequivalent halogen peaks 1 and 5 were found distinctly different, the maximum values being in the ratio 1/1.6, and the number of electrons associated with them were estimated to be 17 and 35. The statement made in the beginning that the present structure has to be of a disordered type in order to conform to the space group $P2_1/c$ has thus been substantiated.

In the case of the corresponding modification of 1,2,4,5-tetrachlorocyclohexane intensity data have been obtained and Fourier maps worked out. The structure of that compound is analogous to that which has been presented in detail here. The isomorphous relationship between the two compounds indicated by the unit cell dimensions has thus been confirmed.

The author wishes to thank *Universitetets Jubileumsfond til Næringsveienes Oppkomst* for financial aid.

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Received May 12, 1954.