

Crystal Structure of *trans* 1,4-Chlorobromocyclohexane

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It has been known for many years that dibromocyclohexane m.p. 112° C and diiodocyclohexane m.p. 142° C are the 1,4-*trans* compounds^{1,2}. The dichlorocyclohexane m.p. 102° C corresponds to these compounds^{1,3}, and the modification of the latter, stable below 12° C, is isomorphous with them³. A further substance, chlorobromocyclohexane m.p. 102° C has recently been prepared and shown to be isomorphous with these three 1,4-dihalogenocyclohexanes³. The space group of all the substances was found to be $P2_1/a$ and the unit cell contains *two* molecules, implying that the molecules themselves have a center of symmetry, a requirement which may easily be fulfilled in the cases where the halogen atoms are both of the same kind, but not in the case of the chlorobromo compound. The crystallographic data of the four substances are as follows (Table 1):

Table 1. Crystallographic data of the *trans* 1,4-dihalogenocyclohexanes.

	<i>a</i>	<i>b</i>	<i>c</i>	β
$C_6H_{10}Cl_2$	11.58	5.36	5.80 Å	105°
$C_6H_{10}ClBr$	11.81	5.52	5.95 Å	103°
$C_6H_{10}Br_2$	11.92	5.56	6.02 Å	103°
$C_6H_{10}I_2$	12.50	5.72	6.20 Å	98°

Although no X-ray reflexions from crystals of the chlorobromo compound have been observed which would indicate that the true lattice constants are larger than those corresponding to the three other dihalogeno compounds, two heavily overexposed rotation diagrams were taken in order to prove the correctness of the unit cell deduced from the existing X-ray data. No indications of additional layer lines could be detected. It therefore appears probable that the structure is of a disordered type, the orientation of the molecules being statistically distributed in the crystal. Earlier examples of the same kind have been reported by Hendricks in the case of *p*-chlorobromobenzene⁴ and Hassel, Wang Lund and Lunde⁵ in the case of 1 κ ,2 κ -dichloro-4 κ ,5 κ -dibromocyclohexane.

As Fourier maps had already been worked out for the dibromo and dichloro compounds, approximate coordinates for the carbon and halogen atoms were

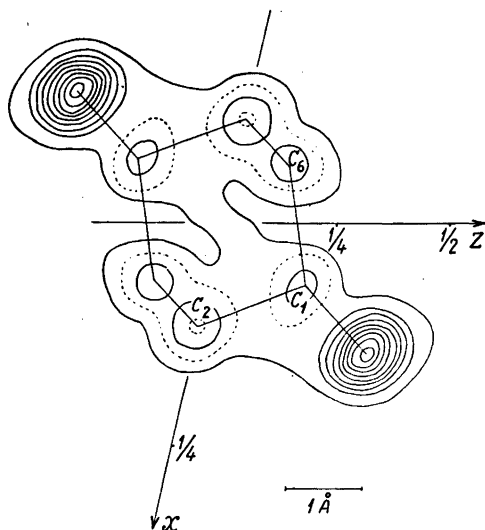


Fig. 1. $C_6H_{10}ClBr$. Electron density map projected along the b axis. Contours at intervals of $2 e. \text{Å}^{-2}$ for the C-atoms, at intervals of $4 e. \text{Å}^{-2}$ for the Cl-Br-atoms. The first contour line is $2 e. \text{Å}^{-2}$.

available and thus the signs of the greater part of the amplitudes could be easily obtained. Fourier maps could therefore be worked out without much trouble. In Figures 1 and 2 these electron density maps corresponding to projection along the b and c axes, respectively, are reproduced. The atomic

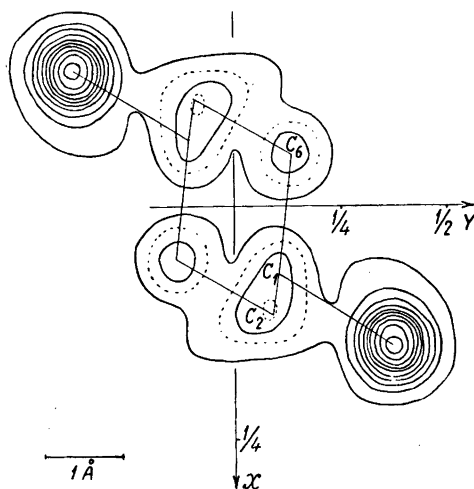


Fig. 2. $C_6H_{10}ClBr$. Electron density map projected along the c axis. Contours at intervals of $2 e. \text{Å}^{-2}$ for the C-atoms, at intervals of $4 e. \text{Å}^{-2}$ for the Cl-Br-atoms. The first contour line is $2 e. \text{Å}^{-2}$. Scale as in Fig. 1.

coordinates (*cf.* Table 2) are generally in good agreement with coordinates earlier found in this laboratory for the dibromo compound (A. Bergskaug)⁶, the dichloro compound (O. Bowitz)⁷, and the iodine coordinates of the diiodo compound (Halmøy and Hassel)¹. Some deviations are observed in the *y*-coordinate of the second carbon atom (C₂), but the overlapping of the C₁ and C₂ atoms makes an exact determination of the *y*-coordinates rather difficult in any case.

Table 2. *a.* Atomic coordinates as fractions of the corresponding cell edge, of the *trans* 1,4-dihalogenocyclohexanes.

	Atom	<i>x</i>	<i>y</i>	<i>z</i>
C ₆ H ₁₀ Cl ₂	Cl	0.148	0.369	0.378
	C ₁	0.071	0.099	0.205
	C ₂	0.123	0.106	0.002
	C ₆	-0.061	0.134	0.118
C ₆ H ₁₀ ClBr	Cl, Br	0.148	0.370	0.381
	C ₁	0.072	0.101	0.201
	C ₂	0.117	0.089	-0.013
	C ₆	-0.060	0.134	0.119
C ₆ H ₁₀ Br ₂	Br	0.148	0.371	0.383
	C ₁	0.075	0.113	0.223
	C ₂	0.116	0.108	-0.024
	C ₆	-0.060	0.134	0.139
C ₆ H ₁₀ I ₂	I	0.150	0.365	0.385

b. Bond lengths in chlorobromocyclohexane as derived from the coordinates given above.

Cl, Br—C ₁	1.93 Å
C ₁ —C ₂	1.49 Å
C ₁ —C ₆	1.54 Å
C ₂ —C ₆	1.48 Å

Table 3 contains observed and calculated *F*-values. The calculated values were obtained on the basis of Thomas-Fermi and Hartree *f*-curves for bromine and chlorine atoms using a curve for all halogen atoms which is the arithmetic mean of the two *f*-curves. In general, the agreement between calculated and observed values is satisfactory, the reliability factor being 0.15 (*h0l*) and 0.14 (*hk0*). Still, it may be questioned if the way in which the *f*-values have been derived can be regarded as fully satisfactory. The procedure adopted implies that all halogen atoms have the same scattering power, a condition which is fulfilled only if the halogen atoms are quite irregularly distributed over the available positions. It might happen that halogen atoms in direct contact are to some extent preferably either of the same or of the opposite kind, two atoms belonging to the same molecule being necessarily always of different kinds. The reflexions which should be expected to be most sensitive to effects of the kind just mentioned are those whose amplitudes have opposite signs in the dichloro and the dibromo compound. Only *two* such reflexions have been found, namely 200 and 110. As a matter of fact the relative agreement between

Table 3. Comparison of observed and calculated structure factors.

<i>hkl</i>	<i>F</i> _{obs}	<i>F</i> _{calc}	<i>hkl</i>	<i>F</i> _{obs}	<i>F</i> _{calc}
200	3.3	+0.1	$\bar{2}04$	<2.1	-0.7
400	20.4	-18.3	$\bar{4}04$	4.5	+5.3
600	5.9	+6.1	$\bar{6}04$	3.7	-4.8
800	2.7	+2.4	$\bar{8}04$	<2.5	-1.3
1000	6.1	-5.9	$\bar{10}04$	3.9	+5.1
1200	<2.3	+0.6	$\bar{12}04$	<2.1	-0.1
1400	1.6	+2.3	$\bar{14}04$	<1.2	-2.0
001	4.3	-7.2	005	6.3	+1.6
201	7.7	-6.6	205	2.5	+1.6
401	12.7	+12.0	405	6.0	-5.0
601	3.5	-3.1	605	<2.2	+0.3
801	7.7	-6.7	805	1.6	+2.0
1001	4.4	+3.5	$\bar{2}05$	3.9	-4.6
1201	<2.2	+1.6	$\bar{4}05$	2.4	-2.7
$\bar{14}01$	<1.2	-1.8	$\bar{6}05$	4.4	+5.4
$\bar{2}01$	20.1	+22.7	$\bar{8}05$	<2.3	-0.3
$\bar{4}01$	<1.4	+1.9	$\bar{10}05$	2.2	-2.9
$\bar{6}01$	15.5	-14.9	$\bar{12}05$	<1.7	+1.2
$\bar{8}01$	2.2	+2.5	006	<2.4	-0.3
$\bar{10}01$	5.0	+4.5	206	3.2	-3.2
$\bar{12}01$	3.8	-3.3	406	<1.9	+0.8
$\bar{14}01$	<1.7	-0.6	606	<1.3	+0.4
002	2.4	+2.0	206	4.2	+4.5
202	12.6	+14.4	$\bar{4}06$	<2.4	-0.8
402	8.4	-7.7	606	2.3	-2.3
602	5.3	-4.4	806	2.0	+2.5
802	8.2	+7.1	1006	<1.7	+0.2
1002	<2.4	+0.5	007	<1.7	-0.9
$\bar{12}02$	2.7	-3.1	207	<1.3	+1.7
$\bar{2}02$	14.6	-19.3	$\bar{2}07$	2.4	-1.5
$\bar{4}02$	3.2	+4.3	$\bar{4}07$	1.8	+2.4
$\bar{6}02$	8.9	+8.4	$\bar{6}07$	<1.7	+0.9
$\bar{8}02$	4.9	-5.7	807	<1.4	-1.6
$\bar{10}02$	<2.4	-0.6	110	3.0	-0.4
$\bar{12}02$	2.4	+3.3	210	17.0	-16.4
1402	<1.7	-1.1	310	12.6	+12.2
003	7.8	+7.0	410	8.3	+7.3
203	10.2	-9.6	510	3.4	-2.7
403	<2.2	+0.0	610	8.0	+7.6
603	8.1	+7.8	710	9.3	-8.9
803	<2.5	-1.0	810	6.0	-5.8
1003	2.2	-2.2	910	3.0	+2.7
1203	<1.3	+0.9	1010	<2.2	-0.5
$\bar{2}03$	3.1	+3.5	1110	<2.2	+2.3
$\bar{4}03$	13.2	-14.5	1210	2.3	+3.3
$\bar{6}03$	<2.1	+0.2	1310	2.0	-2.8
$\bar{8}03$	8.5	+10.0	1410	<1.4	-1.5
$\bar{10}03$	<2.5	-1.2	020	<1.3	+0.4
$\bar{12}03$	<2.3	-2.5	120	14.1	12.2
1403	<1.6	+1.5	220	<1.3	+0.7
004	8.4	-8.2	320	5.0	+3.3
204	4.0	+4.1	420	<1.6	-0.2
404	4.9	+4.8	520	11.4	-11.6
604	4.3	-3.7	620	<1.8	-1.2
804	<2.3	-0.4	720	4.3	+4.7
1004	9.1	+2.2	820	<2.1	+0.1

<i>hkl</i>	F_{obs}	F_{calc}	<i>hkl</i>	F_{obs}	F_{calc}
9 2 0	5.9	+6.8	8 4 0	<2.2	-1.1
10 2 0	<2.2	+0.8	9 4 0	<2.1	-0.5
11 2 0	3.3	-4.7	10 4 0	2.9	+4.9
12 2 0	<1.9	-0.2	11 4 0	<1.5	+0.4
13 2 0	<1.6	-1.8	12 4 0	<1.1	-0.6
14 2 0	<1.1	-0.2	1 5 0	<2.2	+0.4
1 3 0	5.5	+5.2	2 5 0	4.6	+4.5
2 3 0	9.7	-10.0	3 5 0	2.8	-3.4
3 3 0	9.7	-9.1	4 5 0	3.3	-3.7
4 3 0	3.0	+3.0	5 5 0	<2.2	+1.1
5 3 0	<2.0	+0.2	6 5 0	2.7	-3.0
6 3 0	4.3	+4.8	7 5 0	2.5	+3.3
7 3 0	6.9	+6.7	8 5 0	2.3	+3.2
8 3 0	3.0	-3.2	9 5 0	<1.6	-1.1
9 3 0	<2.2	-1.8	10 5 0	<1.2	+0.2
10 3 0	<2.1	-0.3	0 6 0	<2.0	+0.2
11 3 0	<2.0	-2.4	1 6 0	2.5	-3.8
12 3 0	<1.7	+2.2	2 6 0	<2.0	-0.5
13 3 0	<1.2	+2.3	3 6 0	<1.9	-1.5
0 4 0	13.1	-13.0	4 6 0	<1.8	-0.0
1 4 0	3.0	-2.4	5 6 0	2.1	+3.7
2 4 0	<2.1	+1.1	6 6 0	<1.5	+1.1
3 4 0	2.3	-2.3	7 6 0	<1.3	-1.2
4 4 0	6.6	+7.6	8 6 0	<0.8	-0.0
5 4 0	<1.7	+0.8	1 7 0	<1.0	-1.6
6 4 0	3.6	-4.1	2 7 0	<0.9	+2.1
7 4 0	<2.2	+0.3			

observed and calculated intensities is not good for these reflexions; the calculated intensity of 200 would be in much better agreement with the observed value if the f -curve of either only chlorine or only bromine had been employed. The same holds true for the 110 reflexion. (Table 4.)

Table 4. Calculated and observed F -values for 200 and 110 reflexions, the former in the case of two Cl, two Br and two "Artificial" atoms with a diffraction power midway between Cl and Br.

	Calculated:	Observed:
200	F_{Cl}	+ 2.63
	$F_{\frac{\text{Cl}+\text{Br}}{2}}$	+ 0.12
	F_{Br}	- 2.37
110	F_{Cl}	+ 3.03
	$F_{\frac{\text{Cl}+\text{Br}}{2}}$	- 0.41
	F_{Br}	- 3.86

The problem just mentioned might perhaps be attacked with success by studying corresponding intensities from mixed crystals containing nearly equimolecular amounts of the two dihalogeno compounds. Owing to lack of material such investigations have so far not been started. Corresponding studies in the case of p -dichlorobenzene, p -dibromobenzene and p -chlorobromobenzene have also been planned.

SUMMARY

The crystal structure of *trans* 1,4-chlorobromocyclohexane³ has been determined and electron density projections along two of the principal axes worked out. The apparent crystallographic equivalency of chlorine and bromine atoms in the crystal suggested that structure factors could be evaluated on the basis of a single *f*-curve for all halogen atoms: the arithmetic mean of curves for chlorine and bromine atoms. The reliability factors thus obtained were actually satisfactory for both projections. However the intensity of two reflections — 200 and 110 — were much stronger than calculated. For both these reflexions the structure amplitude of the dichloro and dibromo compound is nearly the same, but the sign is reversed. These findings seem to indicate that an evaluation of the structure amplitudes of the chlorobromo compound assuming a true statistical distribution of chlorine and bromine atoms over all available halogen positions is not strictly correct.

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