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The Crystal Structure of 1,2,3,4-Tetrabromocyclohexane, M. P. 142° C

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For some time chemical investigations dealing with 1,2,3,4-tetrahalogenocyclohexanes have been carried out in this laboratory. A report of the results obtained will be published in the near future [1]. In the course of this work three different tetrabromocyclohexanes have been isolated by adding bromine to cyclohexadiene-1,3. The melting points are 89°—90° C, 142° C and 155°—156° C respectively. It would be expected that one of these is identical with the compound melting at 140°—141° C reported by Zelinsky and Gorsky [2]. Harries [3] prepared a compound of m. p. 89°—90° C and obtained also a substance melting about 140° C. By recrystallization, however, he succeeded in raising the melting point of the latter to 155°—156° C. This result indicated at that time some doubt about the existence of the compound melting at 142° C. A detailed study of this isomer was therefore regarded to be most interesting.

First of all, preliminary X-ray investigations of all three compounds have been carried out and the data are given in Table 1.

Table 1. X-ray data for isomers of 1,2,3,4-$C_6H_8Br_4$.

M. p.	a	b	c	β	Calc. density gcm^{-3}	Number of molecules per unit cell	Space group
89—90° C	14.21	10.22	7.91	121°	2.70	4	$P2/a$ or Pa
142° C	11.28	22.55	7.89		2.65	8	Fdd
155—156° C	9.91	8.52	8.06	133°	2.67	2	$P2_1$

The values of calculated density correspond well to those measured for the 1$\varkappa$, 2$\varkappa$, 4ε, 5ε [4] — and 1$\varkappa$, 2$\varkappa$, 4$\varkappa$, 5$\varkappa$ [5]-tetrabromocyclohexanes, respectively

2.66 g cm^{-3} and 2.74 g cm^{-3}. The compound melting at 142° C appeared to be the most suitable one for an X-ray analysis.

Tetrabromocyclohexane with m. p. 142° C crystallizes in two different shapes. From ligroin fine needles elongated along [001] were obtained and from methanol the crystals are orthorhombic pyramids with (010) as base. The X-ray investigation shows that both forms have the same lattice.

The unit cell dimensions, measured from rotation and Weissenberg photographs, are given in Table 1. With eight molecules in the unit cell these values give a calculated density of 2.65 g cm^{-3}. Oscillation and Weissenberg photographs show that the crystals belong to the orthorhombic system. The study of systematic extinctions gives the result that only the following reflexions are present:

(hkl) when all indices are even or all odd
($hk0$) when $h = 2n$ and $k = 2n$
($0kl$) when $k = 2n$, $l = 2n$ and $k + l = 4n$
($h00$) when $h = 4n$

This leads to a face-centred lattice and without ambiguity to the space group Fdd which has a sixteen-fold general position. The molecule must therefore possess the point symmetry, *viz.* a twofold axis associated with the eight-fold special positions.

From this follows that the molecule must possess a "chair"-like carbon ring, and the configuration for the bromine atoms must be either $1\varkappa$, $2\varkappa$, $3\varkappa$, $4\varkappa$ or $1\varkappa$, 2ε, 3ε, $4\varkappa$ respectively 1ε, $2\varkappa$, $3\varkappa$, 4ε, the two latter ones being transformed into each other by a conversion of the carbon ring.

For the determination of the structure the intensities of all reflexions ($hk0$) and ($0kl$) obtainable with Cu-K radiation were estimated visually by comparison with a standard scale and using the multiple film method. The f-values used in computing structure factors were those of the International Tables, with temperature factors to be mentioned later. No correction for absorption has been introduced, the crystals used in the investigation being very small.

In order to decide between the three possibilities mentioned above first of all a Patterson projection on (001) was computed. The resulting map is reproduced in Fig. 1, which corresponds to one sixteenth of the unit cell. The points marked with squares are the projections of terminating points of the vectors between bromine atoms in the final xy-projection.

The map shows two dominating peaks situated in ($\frac{1}{4}$, 0.114) and (0.083, $\frac{1}{4}$). These peaks are obviously due to vectors from a bromine atom in (x, y, z) to two other equivalent ones in ($\frac{1}{4} + x$, $\frac{1}{4} - y$, $\frac{1}{4} + z$) and ($\frac{1}{4} - x$, $\frac{1}{4} + y$, $\frac{1}{4} + z$) respectively, the projections of the corresponding vectors having the compo-

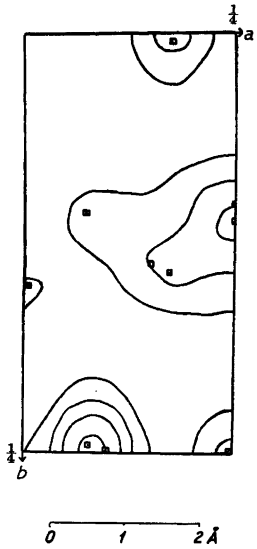

Fig. 1. Patterson projection on (001).

nents ($\frac{1}{4}$, $\frac{1}{4} - 2y$, $\frac{1}{4}$) and $\frac{1}{4} - 2x$, $\frac{1}{4}$, $\frac{1}{4}$). This leads to the coordinates $x = 0.083$, $y = 0.068$. Now in an "ideal" structure with tetrahedral angles the distance from the twofold axis to a bromine atom in $2x$-position is 1.69Å taking the C—C and C—Br bond lengths to be respectively 1.54 Å and 1,94 Å. Assuming the x- and y-coordinates found above to belong to one bromine atom, the distance of this atom from the twofold axis is 1.80 Å. It might therefore be assumed that the molecule contains a bromine atom in $2x$-position when some deformation from an "ideal" structure is taken into account. With a $2x$-bromine atom in the point thus found, the Patterson peak in (0.175, 0) may be interpreted as resulting from a vector between $1x$ and $2x$ bromine atoms. In an "ideal" structure the corresponding vector has the x- and y-components (0.150, 0.030). This preliminary investigation based on the Patterson projection should thus indicate a $1x$, $2x$, $3x$, $4x$-configuration with some deformations of the molecule from an "ideal" model.

Due to extensive overlapping of vector peaks, however, a Patterson projection is difficult to interprete uniquely. It was therefore felt that the above considerations had to be supported by a more systematic treatment of the different possibilities. Assuming an "ideal" structure of one of those having a twofold axis, we have in the xy-projection a one-parameter problem, the parameter being the angle α which a representative line in the molecule makes with the a-axis, say.

For the three different possible structures the variation of the $F(hk0)$'s with this angle was determined in the whole range of α-values. The desired

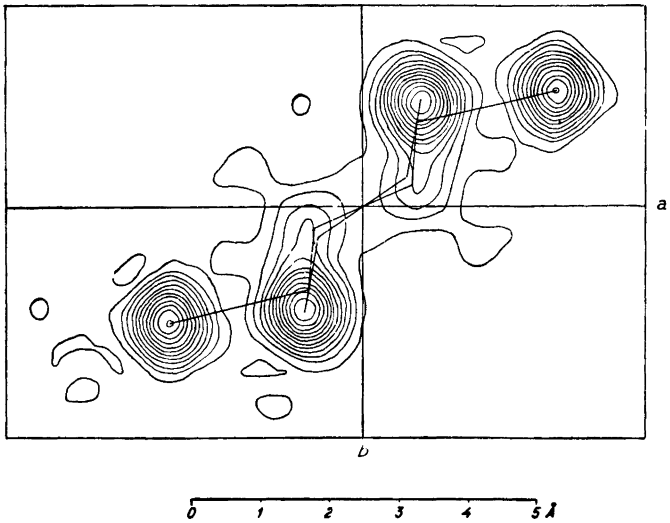

Fig. 2. Fourier projection on (001).

agreement between observed and calculated F-values was obtainable only for the $1x$, $2x$, $3x$, $4x$-configuration and for an orientation of the molecule very nearly the same as that found by means of the Patterson projection.

This preliminary structure could then serve as the base for a Fourier projection on (001). The number of $hk0$-reflexions used in the analysis was 49. With a few exceptions the signs of the structure factors were determined by the bromine atoms. In fact, in the first synthesis the contribution of the carbon atoms was omitted, but their introduction at a later stage gave a better agreement between calculated and observed intensities and a few sign changes.

It is impossible in this projection to locate the carbon atoms with any degree of certainty on account of the overlapping of the neighbouring large peak due to a bromine atom. The presence of the two carbon atoms C_2 and C_6, which in the "ideal" model have the same x- and y-coordinates, appears as an extension of this same bromine peak. The projection in the (100)-plane gives a little more information on this point. As to the hydrogen atoms their effect is so negligible that they have not been taken into account at all.

In order to improve the agreement between observed and calculated $|F|$-values for the reflexions with larger ϑ-values, a temperature factor of $B = 5.78$ Å^2 was introduced. The agreement factor ($\Sigma|\Delta F/F|$) for the final xy-projection was found to be 0.20. In Fig. 2 the electron density map is reproduced.

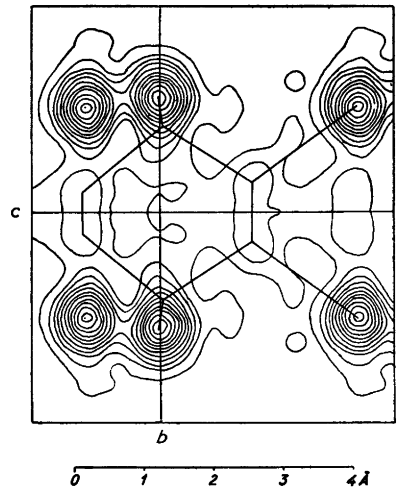

Fig. 3. Fourier projection on (100).

As to the determination of the z-parameters a projection on (100) appeared to be more convenient than one on (010) which gives larger amount of overlapping of different peaks than the former. The projection of the structure on (100) does not contain a center of symmetry and phase angles had therefore to be computed. On account of the extinction rule $k + l = 4n$ only 33 reflexions were used in this projection.

As a starting point served a structure where the y-coordinates of the bromine atoms were taken from the xy-projection while their z-coordinates as well as all the coordinates for the carbon atoms were derived from an "ideal" model of the molecule in a position approximately determined by the x- and y-coordinates of the bromine atoms. This trial structure proved to be nearly correct as to the position of the bromine atoms, the first Fourier synthesis giving no change in their coordinates. The presence of the carbon atoms C_2 and C_6 appears as small peaks well separated from those due to the bromine atoms. The ordinary procedure of successive approximations was followed until the changes in the phase angles were insignificant. As in the xy-projection the hydrogen atoms have not been taken into account. Use has been made of a temperature factor $B = 3.31$ Å^2, the value of which was determined by the curve showing the variation of $|F_{obs}/F_{calc}|$ with ϑ. For the final agreement factor $\Sigma|\Delta F/F|$ the value 0.20 was obtained for this projection too.

Fig. 3 gives the electron density map of a part of the structure on (100). In Figs. 4 and 5 are reproduced schematic projections on (001) and (100) respectively, showing the mutual arrangement of the molecules whose centres

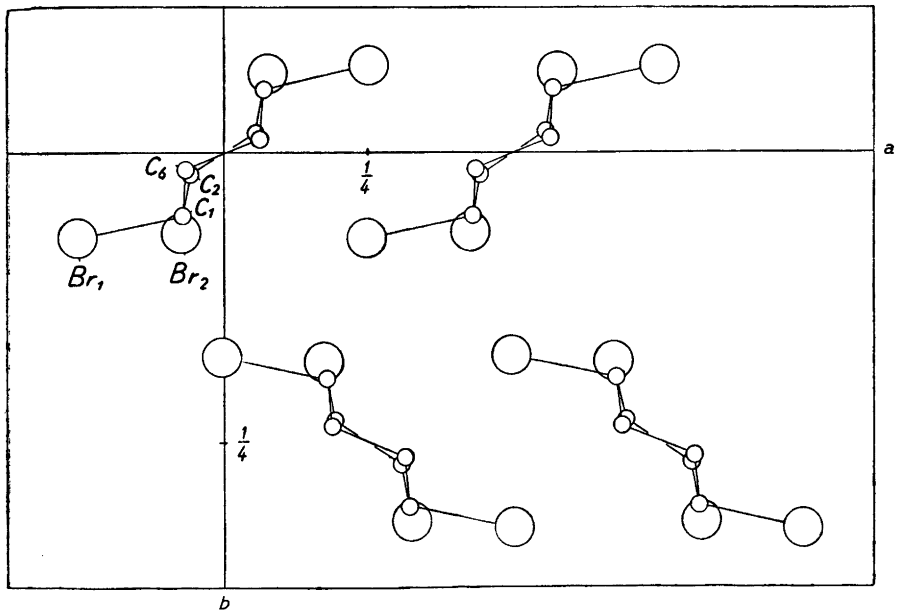

Fig. 4. 1x, 2x, 3x, 4x—$C_6H_8Br_4$. Projection of the structure on (001).

are situated in (0, 0, z_0), ($\frac{1}{4}$, $\frac{1}{4}$, $\frac{1}{4} + z_0$), ($\frac{1}{2}$, 0, $\frac{1}{2} + z_0$) and ($\frac{3}{4}$, $\frac{1}{4}$, $\frac{3}{4} + z_0$), the origin being chosen in such a way that z_0 is nearly zero.

In both projections the peaks due to bromine atoms are well defined and these atoms can thus be given rather reliable coordinates. As to the carbon atoms the situation is different. The *yz*-projection gives the *y*- and *z*-coordinates of C_2 and C_6, while their *x*-coordinate as well as the coordinates for the carbon atom C_1 are not determinable by means of the maps. The assumption that the C—C bond length is 1.54 Å allows a computation of the *x*-coordinates for C_2 and C_6, while the coordinates given to C_1 are those derived from an "ideal" carbon ring. This procedure gives a mean C—Br bond length of 1.99 Å. In Table 2 the coordinates of crystallographically independent atoms are listed. Table 4 gives the observed and calculated $|F|$-values for the (*hk*0) and (0*kl*) reflexions.

Table 2. Coordinates for bromine and carbon atoms.

	x	*y*	*z*
Br_1	— 0.252	0.074	0.002
Br_2	— 0.075	0.069	— 0.360
C_1	— 0.071	0.055	— 0.004
C_2	— 0.057	0.019	— 0.167
C_6	— 0.063	0.013	0.144

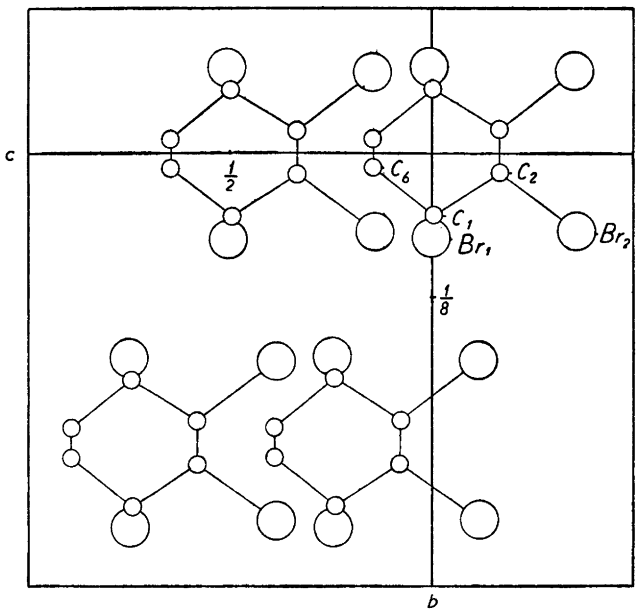

Fig. 5. 1x, 2x, 3x, 4x—$C_6H_8Br_4$. Projection of the structure on (100).

In spite of the non rigorous localization of carbon atoms there is no doubt that the configuration of bromine atoms is 1x, 2x, 3x, 4x. Fig. 6 shows a model of this tetrabromocyclohexane molecule.

As to the deviation of the molecule from an "ideal" model no statement about deformation of valency angles can be made on account of the uncertain positions of the carbon atoms. The Br—Br distances within the same molecule may nevertheless give an indication of the directions in which the deformations take place. The Br_1—Br_2 and Br_2—Br_3 distances are 3.49 Å and 3.54 Å respectively, while the "ideal" value for both is 3.38 Å when the C—C and C—Br bond lengths are taken to be 1.54 Å and 1.94 Å. The Br_1—Br_4 distance has, however, decreased from an "ideal" value of 6.62 Å to 6.59 Å and the Br_1—Br_3

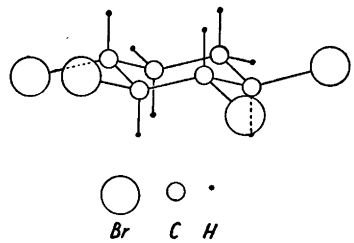

Fig. 6. Model of a molecule of 1x, 2x, 3x, 4x—$C_6H_8Br_4$.

distance correspondingly from 5.69 Å to 5.67 Å. A probable deformation is thus mainly composed of two parts:

1. In order to increase the distance between the atoms Br_2 and Br_3, these atoms are displaced oppositely in the directions of the three-fold inversion axis of the carbon ring.

2. Perpendicularly to this axis the atoms Br_1 and Br_4 are displaced in such a way that their distance from the respective neighbouring bromine atoms is increased.

A consideration of the distances between atoms belonging to neighbouring molecules allows some conclusions to be drawn about the dominating van der Waals' forces. The shortest Br—Br distance of this type has the length of 3.80 Å. It would be of interest to know the distances between hydrogen and bromine atoms belonging to different molecules, but it is impossible to locate hydrogen atoms by means of the maps. Assuming, however, tetrahedral angles between the C—C and C—H bonds and a C—H bond length of 1.08 Å, "ideal" coordinates for the hydrogen atoms may be calculated. The shortest H—Br distance thus found is 2.88 Å. In Table 3 some of the distances between atoms belonging to neighbouring molecules are listed. The first column gives the coordinates for the symmetry center of the carbon ring ($z_0 = -0.09$) in the molecules concerned. In the second column those atoms are indicated between which the distance in column three is computed.

Table 3. Intermolecular atomic distances.

$(0, 0, z_0)$ $(\frac{1}{2}, 0, \bar{\frac{1}{2}} + z_0)$	$Br_{2\varkappa}$ $Br_{1\varkappa}$	3.80 Å
$(0, 0, z_0)$ $(0, 0, 1 + z_0)$	$H_{6\varkappa}$ $Br_{2\varkappa}$	3.06 Å
$(0, 0, z_0)$ $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4} + z_0)$	$H_{1\varepsilon}$ $Br_{2\varkappa}$	2.99 Å
$(0, 0, z_0)$ $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4} + z_0)$	$H_{1\varepsilon}$ $Br_{1\varkappa}$	2.88 Å

These correspond reasonably well to normal van der Waals' distances. It may therefore be concluded that the cohesion of the lattice in the a-direction is due, in the main, to forces acting between neighbouring bromine atoms. In other directions the dominating forces are those between hydrogen and bromine atoms.

Table 4. Observed and calculated $|F|$-values.

(*hkl*)	$\|F\|_{obs}$	$\|F\|_{calc}$	(*hkl*)	$\|F\|_{obs}$	$\|F\|_{calc}$
0. 4.0	0	7	10. 2.0	6	7
0. 8.0	65	70	10. 4.0	8	11
0.12.0	45	37	10. 6.0	8	6
0.16.0	24	26	10. 8.0	0	2
0.20.0	24	26	10.10.0	0	0
0.24.0	0	6			
0.28.0	4	10	12. 0.0	8	9
			12. 2.0	0	2
2. 2.0	5	3	12. 4.0	0	2
2. 4.0	43	42	12. 6.0	0	2
2. 6.0	20	21	12. 8.0	5	7
2. 8.0	0	3			
2.10.0	5	4			
2.12.0	14	15	0. 2.2	37	37
2.14.0	6	7	0. 6.2	57	48
2.16.0	6	5	0.10.2	10	11
2-18.0	8	6	0.14.2	24	29
			0.18.2	9	6
4. 0.0	22	25	0.22.2	9	12
4. 2.0	31	32	0.26.2	6	6
4. 4.0	13	8			
4. 6.0	23	22	0. 0.4	10	10
4. 8.0	12	14	0. 4.4	9	8
4.10.0	14	18	0. 8.4	8	11
4.12.0	16	12	0.12.4	6	5
4.14.0	0	1	0.16.4	11	6
4.16.0	0	2	0.20.4	0	3
4.18.0	11	11	0.24.4	8	6
6. 2.0	38	35	0. 2.6	31	25
6. 4.0	10	8	0. 6.6	24	25
6. 6.0	35	36	0.10.6	6	6
6. 8.0	0	1	0.14.6	16	21
6.10.0	6	7	0.18.6	5	4
6.12.0	0	2	0.22.6	6	10
6.14.0	20	22			
6.16.0	0	2	0. 0.8	30	22
			0. 4.8	4	5
8. 0.0	0	2	0. 8.8	19	17
8. 2.0	7	6	0.12.8	7	9
8. 4.0	6	5	0.16.8	7	8
8. 6.0	6	4			
8. 8.0	0	2	0.2.10	4	2
8.10.0	0	5			
8.12.0	0	3			

SUMMARY

The crystal structure of 1,2,3,4-tetrabromocyclohexane of m. p. 142° C, obtained from cyclohexadiene-1,3 and bromine, has been determined. The bromine atoms occupy the positions: $1\varkappa$, $2\varkappa$, $3\varkappa$, $4\varkappa$. Deviations from the "ideal" structure and the intermolecular atomic distances have been considered.

I wish to thank Prof. O. Hassel for placing samples of the 1,2,3,4-$C_6H_8Br_4$ compounds at my disposal and also for his continued interest in the investigation. Further I should like to express my gratitude to *A/S Lilleborg Fabriker* for financial assistance from *A/S Lilleborg Fabrikers Jubileumsgave.*

REFERENCES

1. Hassel, O., and Lunde, K. *Acta Chem. Scand.* (1950). To be published.
2. Zelinsky, N., and Gorsky, A. *Ber.* **41** (1908) 2483.
3. Harries, C. *Ber.* **45** (1912) 809.
4. Halmøy, E., and Hassel, O. *J. Am. Chem. Soc.* **61** (1939) 1601.
5. Haak, F. A. *De bereidning en structuur van cyclohexadiëen-1,4 en van enige derivaten.* Firma P. Harte, Bergen op Zoom (1948).

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