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The Crystal Structure of β-1, 2, 4, 5-Tetrabromocyclohexane

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The crystal structure of β-1, 2, 4, 5-tetrabromocyclohexane has been determined. Cell dimensions are $a = 7{\cdot}23$, $b = 12{\cdot}32$, $c = 6{\cdot}36$ Å, $\beta = 110°\ 30'$. The space group is $P2_1/c$. Three projections of electron density are given. The carbon six-ring has the chair configuration; all bromine atoms are placed equatorially.

1. Introduction and results

The addition of bromine to cyclohexadiene-1, 4 yields two tetrabromocyclohexanes, $C_6H_8Br_4$. The main component, melting at 188° C. (corr.), was investigated by Halmøy & Hassel (1939), and was proved to have the spatial structure 1ϵ, 2ϵ, 4κ, 5κ ($1p, 2p, 4e, 5e$ in the notation of Pitzer). The other tetrabromocyclohexane, melting at 218° C. (corr.), only a small percentage of which occurs in the crystal mixture, has been described in an earlier communication (Wibaut & Haak, 1948). It was assumed that in this tetrabromide, also, the bromine atoms were attached to the carbon atoms 1, 2, 4 and 5, though this assumption was based on indirect evidence only. As a short notation these two tetrabromides have been called α- and β-1,2,4,5-tetrabromocyclohexane respectively (Haak, 1948, p. 22).

From X-ray analysis the spatial configuration of this isomer has been derived. The space group, $P2_1/c$, and the number of molecules in the unit cell, 2, require that the molecule has a centre of symmetry, and thus the chair configuration. Moreover, this centre of symmetry in the molecule confirms the assumption that the four bromine atoms are bonded to the carbon atoms 1, 2, 4 and 5 respectively. As the chair configuration of the six-membered carbon ring is not flexible it was possible to calculate the distance from a bromine atom to the centre of the ring in the two possible positions: equatorial and polar.† The bromine distances to the centres of symmetry in the unit cell, calculated from the crystallographically determined bromine parameters, indicate that all bromine atoms are placed equatorially.

Because of the high bromine content (80% by weight) of this compound, and the great scattering power of the bromine atoms compared with that of the carbon atoms, it was not possible to find the exact positions of the later.

2. Crystallographic data, cell dimensions and number of molecules in the cell

Very thin plates were obtained by recrystallization from benzene. A pronounced cleavage along the [001] axis was observed. The crystals are monoclinic. From Weissenberg diagrams about [100], [010] and [001] with Cu K radiation the cell constants were found:

$$a = 7{\cdot}23,\quad b = 12{\cdot}32,\quad c = 6{\cdot}36\ \text{Å},\quad \beta = 110°\ 30'.$$

The density was determined by the suspension method in a solution of $ZnBr_2$ in water. The observed value ($2{\cdot}8$ g.cm.$^{-3}$) indicated the presence of two molecules in the cell, with which number an X-ray density of $2{\cdot}96$ g.cm.$^{-3}$ is calculated.

3. Space group

The Weissenberg diagrams of the zero layer line about the a and c axes showed two planes of symmetry, those of the first layer line only one. The diagrams of the zero and first layer lines about the b axis did not contain any planes of symmetry; consequently the crystals have a monoclinic symmetry. The following reflexions were absent:

reflexions ($0k0$) for k odd,
reflexions ($h0l$) for l odd.

Thus the space group is $P2_1/c$.

4. Electron-density projections

Although this compound has a very high bromine content, it was possible, for Weissenberg diagrams about the a and c axes, to prepare crystals small enough for absorption to be neglected (the values of μr in these cases were $0{\cdot}2$ and $0{\cdot}5$ respectively). For Weissenberg diagrams about the b axis a (010) plate was shaped to a cylinder of $0{\cdot}4$ mm. diameter. In this case a correction for the absorption was introduced, assuming the crystal to be exactly cylindrical in shape. The intensities were estimated visually; multiple-film technique was used.

For the approximate bromine parameters the following values were derived from Patterson projections along the three axes:

$$\begin{array}{llll} Br_{I} & x = 90°, & y = 54°, & z = 165°; \\ Br_{II} & x = -100°, & y = 54°, & z = 83°. \end{array}$$

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† The notation equatorial and polar for the two directions of substituents in the chair configuration of the cyclohexane ring was introduced by Pitzer & Beckett (1947). His abbreviations e and p correspond to Hassel's κ and ϵ respectively (Hassel, 1943).

With these values the signs of the Fourier coefficients were determined, and the three Fourier projections were calculated. These and the corresponding projections of the structure are given in Figs. 1–6. From the electron-density maps the following bromine positions were found:

Br_{I}	$x=90°$,	$y=54°$,	$z=165°$;
Br_{II}	$x=-100°$,	$y=54°$,	$z=81°$.

The observed F values for the three projections are in satisfactory agreement with those calculated with these bromine positions and with the following carbon parameters (calculated for the non-distorted molecule model):

C_1	$x=33°$,	$y=34°$,	$z=54°$;
C_2	$x=-38°$,	$y=14°$,	$z=55°$;
C_3	$x=-78°$,	$y=-4°$,	$z=-25°$.

The contribution of the carbon atoms to the F values is very small. The experimental carbon parameters fit in roughly with the calculated carbon positions.

5. Discussion of the structure

The molecule has a centre of symmetry, so the bromine atoms are bound to the carbon atoms 1, 2, 4 and 5, and the carbon has the chair configuration. The required symmetry of the molecule reduces the number of possible spatial arrangements to three, viz.

(*a*) 1*e*, 2*e*, 4*e*, 5*e*,
(*b*) 1*e*, 2*p*, 4*e*, 5*p*,
(*c*) 1*p*, 2*p*, 4*p*, 5*p*.

Since the cyclohexane ring in the chair configuration is rigid, the distances of the bromine atoms to the centre M of the molecule, and also their relative distances, are fixed and can be calculated in the three cases. Starting from an idealized model, having C–C = 1·54 Å, C–Br = 1·91 Å and all valency angles equal to 109° 28′, the following distances were calculated (Br_{I} and Br_{II} bromine atoms on adjacent carbon atoms):

	MBr_{I}	MBr_{II}	$Br_{I}Br_{II}$	$Br_{I}Br_{V}$
(*a*)	3·32 Å	3·32 Å	3·41 Å	5·67 Å
(*b*)	3·32	2·67	3·32	5·04
(*c*)	2·67	2·67	4·66	2·62

On the other hand, these distances can be computed from the bromine positions derived from the Fourier projections. Disregarding the carbon positions indicated in these maps, two centres of symmetry in the cell may coincide with the centre of the molecule, viz.

(*A*) $x=0$, $y=0$, $z=0$;
and (*B*) $x=0$, $y=0$, $z=180°$.

For these two cases the following distances are found:

	MBr_{I}	MBr_{II}	$Br_{I}Br_{II}$	$Br_{I}Br_{V}$
(*A*)	3·39 Å	3·38 Å	3·53 Å	5·82 Å
(*B*)	2·68	2·85	3·53	4·20

It is clear that case (*A*) is in agreement with the configuration (*a*); accordingly, in this compound all bromine atoms are placed equatorially, and the centre of the molecule lies on $x=0$, $y=0$, $z=0$, in accordance with the observed positions of the carbon atoms. The small deviations of the observed bromine distances

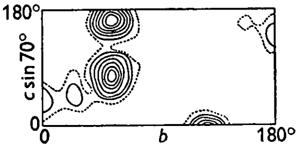

Fig. 1.

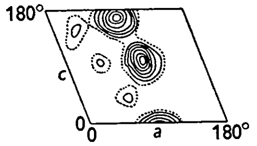

Fig. 2.

Fig. 1. Electron-density projection on the (100) plane.
Fig. 2. Electron-density projection on the (010) plane.

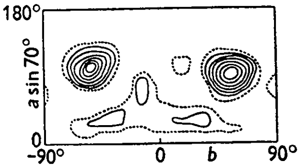

Fig. 3. Electron-density projection on the (001) plane.

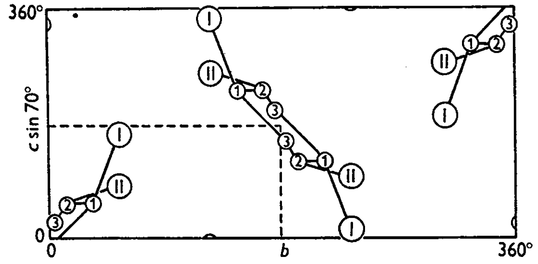

Fig. 4. Projection of the structure on the (100) plane.

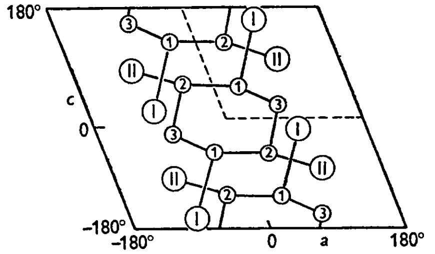

Fig. 5. Projection of the structure on the (010) plane.

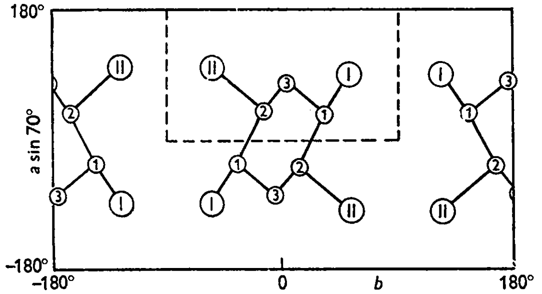

Fig. 6. Projection of the structure on the (001) plane.

from those calculated may be due to a slight distortion of the molecule. However, the unreliability of the observed carbon positions does not justify a further speculation into the nature of this distortion.

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References

HAAK, F. A. (1948). Thesis, Amsterdam.

HALMØY, E. & HASSEL, O. (1939). *J. Amer. Chem. Soc.* **61**, 1601.

HASSEL, O. (1943). *Tidsskr. Kemi Bergv. Met.* **5**, 32.

PITZER, K. S. & BECKETT, C. W. (1947). *J. Amer. Chem. Soc.* **69**, 977.

WIBAUT, J. P. & HAAK, F. A. (1948). *Rec. Trav. chim. Pays-Bas*, **67**, 91.

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The Structure of $TiBe_{12}$†

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$TiBe_{12}$ is hexagonal with $a_0 = 29{\cdot}44$, $c_0 = 7{\cdot}33$ Å, $Z = 48$. There is a pseudo-cell, however, with $A_0 = 4{\cdot}23$, $C_0 = 7{\cdot}33$ Å, $Z = 1$, one Ti per pseudo unit at 0, 0, 0 or 0, 0, $\frac{1}{2}$, and it is the alternation between these two positions which leads to the larger cell. Idealized beryllium positions have been found for the pseudo-cell.

The structure is disordered, and though the general reason for the disorder is apparent, the particular type of disorder observed has not been explained. The structure leads to an unusual set of absences.

1. Introduction

The structures of a number of alloys of high beryllium content have recently been determined. Most of these proved to be $M\mathrm{Be}_{13}$ compounds, and were found by Baenziger & Rundle (1949) to have the cubic $NaZn_{13}$ structure (Ketelaar, 1937; also Zintl & Haucke, 1937). A titanium compound, orginally thought to be $TiBe_{13}$, was found by Baenziger (1947) to have a hexagonal lattice. Zero- and third-layer Weissenberg diagrams, which are representative of the even and odd hexagonal reciprocal-lattice nets of $TiBe_{12}$, are shown in Fig. 1. The reflections appearing in the even-layer lines correspond to the centers of the hexagons in the odd-layer lines. The absences seemed sufficiently unusual to warrant an attempt at a complete structural determination.

2. Experimental procedure

Samples of $TiBe_{12}$ were obtained by heating titanium–beryllium mixtures of approximately 1:15 atomic ratio to about 1400° C. in an induction furnace. One sample obtained in this way had a small cavity in the center into which hexagonal needles extended. There seemed to be only small amounts of a second phase present, so presumably the compound contains only a little less beryllium than $TiBe_{13}$. A satisfactory chemical analysis of the compound has not been obtained because of the difficulty in obtaining adequate samples known to be of one phase.

Needles from the central cavity were easily separated from the matrix, and several, about 1 mm. in length and 0·05–0·1 mm. in diameter, were chosen for examination by X-ray diffraction. The face development on the needles proved to be (100), with end-face generally unobservable.

The following Weissenberg and precession photographs were made:

Cu *Kα* radiation:	Weissenberg (*hk*0) to (*hk*5) and (*h*0*l*).
Mo *Kα* radiation:	Weissenberg (*hk*0) to (*h*, *k*, 10), precession (*hk*0), (*h*0*l*), (*hhl*).
Ag *Kα* radiation:	Weissenberg (*h*0*l*).

The Cu *Kα* pictures were taken by the multiple-film technique. The Mo *Kα* Weissenberg with even *l* indices and the Ag *Kα* pictures were taken as a series of timed exposures at doubled intervals of from $\frac{1}{4}$ to 16 hr.

The intensities of all reflections on the Cu *Kα* films, the Mo *Kα* Weissenberg films of even *l* index, and the (00*l*) reflections from the Ag *Kα* film were estimated by visual comparison of five multiple films (Robertson, 1943) or of six timed exposures. Squares of the structure factors were calculated in the usual fashion. Adsorbtion was quite small for all data, and the temperature corrections were small for the reflections used in the structural determination. Several photographs

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