

**1014.** *Molecular Compounds and Complexes.\* Part I. The Crystal Structure of the Equimolar Molecular Complex of Hexabromobenzene and 1,2,4,5-Tetrabromobenzene.*

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An equimolar molecular complex formed by hexabromobenzene and 1,2,4,5-tetrabromobenzene has been identified and its crystal structure determined by a partial three-dimensional analysis. The components appear to be bonded only by van der Waals interactions. The molecular arrangement is similar to that in hexabromobenzene with stacks of molecules in quasi-hexagonal array. Each stack contains only one molecular component and in this respect the packing differs from that in many polarization-bonded compounds where the stacks contain both components in alternating sequence. The molecules are both planar within the limits of error but  $d(\text{Br} \cdots \text{Br})$  is less in hexabromobenzene ( $3.279 \pm 0.008 \text{ \AA}$ ) than in tetrabromobenzene ( $3.377 \pm 0.004 \text{ \AA}$ ) because in-plane splaying apart of bromine atoms is not possible in hexabromobenzene. The binary phase diagram and the conditions of formation of the molecular complex from solution have been partly determined. The molecular complex decomposes in air at room temperature over a period of weeks by a topotactic reaction: tetrabromobenzene evaporates leaving behind hexabromobenzene crystallites. The hexabromobenzene crystallites on the surface are randomly oriented but those in the interior have the following orientation to the parent lattice:

$$\begin{aligned} [010]_{\text{complex}} &\parallel [010]_{\text{C}_6\text{Br}_6} \\ (001)_{\text{complex}} &\parallel (101)_{\text{C}_6\text{Br}_6} \end{aligned}$$

THE crystal structures of a number of solid phases containing two components have been determined.<sup>1</sup> Most of this work has been concerned with inclusion compounds,<sup>2</sup> polarization-bonded compounds,<sup>3</sup> and hydrogen-bonded structures,<sup>4</sup> and little is known about the molecular arrangements in the complexes where the major intermolecular bonding appears to be due to van der Waals forces. Therefore, when we found by chance (see Experimental section) a crystalline equimolar molecular complex of hexabromobenzene and 1,2,4,5-tetrabromobenzene, we decided that a crystal-structure analysis would be justified. There are also other reasons for interest in this molecular complex. Firstly its analysis would provide dimensions for the two component molecules which are both formally overcrowded. Secondly the molecular complex is not stable in air at room temperature but decomposes over a period of weeks, leaving an oriented, quasi-single crystal residue of hexabromobenzene. Similar topotactic reactions in inorganic<sup>5</sup> and organic<sup>6</sup> crystals have been discussed recently.

A brief account of the present results was given at the Fifth Congress of the International Union of Crystallography.<sup>7</sup>

#### EXPERIMENTAL

*Preparation.*—During the recrystallization of 1,2,4,5-tetrabromobenzene (from British Drug Houses, Laboratory Chemicals Group, batch no. 221030/56201, supplied in 1956) it

\* For two-component (AB) crystals we distinguish between molecular compounds, where  $A \cdots B$  interactions appear to determine the molecular arrangement in the solid, and molecular complexes where either  $A \cdots A$  interactions are most important (*e.g.*, clathrates) or  $A \cdots A$ ,  $A \cdots B$  and  $B \cdots B$  interactions are of approximately equal importance (*e.g.*, the molecular complex described in the present paper). It is planned to present this classification in more detail in a subsequent Paper of this series.

<sup>1</sup> (a) Nyburg, "X-ray Analysis of Organic Structures," Academic Press, New York and London, 1961, pp. 284—296; (b) Kitaigorodskii, "Organic Chemical Crystallography," Consultants Bureau, New York, 1961, pp. 215—219, 502—524.

<sup>2</sup> Hagan, "Clathrate Inclusion Compounds," Reinhold, New York, 1962.

<sup>3</sup> (a) Wallwork, *J.*, 1961, 494; (b) Hassel and Rømming, *Quart. Rev.*, 1962, 16, 1.

<sup>4</sup> Hoogsteen, *Acta Cryst.*, 1959, 12, 822; 1963, 16, 907.

<sup>5</sup> Dent Glasser, Glasser, and Taylor, *Quart. Rev.*, 1962, 16, 343.

<sup>6</sup> Morawetz, Jakabhazy, Lando, and Shafer, *Proc. Nat. Acad. Sci. U.S.A.*, 1963, 49, 789.

<sup>7</sup> Gafner and Herbstein, *Acta Cryst.*, 1960, 13, 1044.

was noticed that small amounts of two other types of crystals were present in the preparations. These crystals were respectively rhombs and thin laths. The rhombs were found only in preparations that had been standing for some months but the laths (which showed straight extinction) appeared at the same time as the 1,2,4,5-tetrabromobenzene needles (which showed oblique extinction). The rhombs were immediately identified as 4,4'-dibromobiphenyl by comparison of suitable Weissenberg photographs with those from an authentic sample.<sup>8</sup> The laths were later identified as the molecular complex under discussion.

The first samples of the laths were obtained by chance in very small quantities and some attention has therefore been given to possible methods of preparation. Equimolar solutions of hexabromobenzene and 1,2,4,5-tetrabromobenzene in benzene, toluene, or xylene do not give the complex either on cooling from 70–80° to room temperature or by allowing the solution to evaporate. Instead the less soluble component, hexabromobenzene, crystallizes out first. Some success was attained with a toluene solution containing a preponderance of tetrabromobenzene (molecular ratio 8 : 1) which was cooled slowly. Determination of optimum conditions for preparation of the laths would require investigation of the ternary system 1,2,4,5-tetrabromobenzene–hexabromobenzene–solvent which we have not attempted. The behaviour of the laths is clearly analogous to that of double salts unstable to water (see, for example, Glasstone<sup>9</sup>).

*Identification of the Laths.*—This was effected from cell dimensions, density (lower limit only determined), identification of the product of thermal decomposition at room temperature, infrared spectra, and crystal-structure analysis. In the early stages of the work insufficient material was available for chemical analysis and later it was felt that chemical analysis was superfluous as physical methods had given unambiguous results.

The cell-dimensions were measured from oscillation and Weissenberg photographs, using Cu-K $\alpha$ -radiation. The following crystallographic data were obtained:  $a = 17.80 \pm 0.02$ ,  $b = 4.01 \pm 0.04$ ,  $c = 14.42 \pm 0.02 \text{ \AA}$ ,  $\beta = 111^\circ 13' \pm 7'$  (by goniometry); {001} and {100} faces are developed;  $D_m > 2.96 \text{ g./c.c.}$

Systematic absences showed the space group to be  $C_{2h}^5 - P2_1/a$ . As the density of tetrabromobenzene is 3.02 g./c.c., the density measurement eliminated the possibility that the laths were a complex of tetrabromobenzene with a less dense molecule. At this stage it was noticed that the originally clear crystals had become cloudy, and further X-ray photography showed the gradual disappearance of the original diffraction pattern and its replacement by a new pattern. This was identified as that of hexabromobenzene by comparison with a photograph from an authentic sample.<sup>10</sup> The thermal decomposition is described in more detail below. It was then clear that hexabromobenzene was one component of the laths.

The unit-cell volume of the laths is 961  $\text{\AA}^3$ , while that of hexabromobenzene is 525  $\text{\AA}^3$  and that of  $\beta$ -1,2,4,5-tetrabromobenzene is 434  $\text{\AA}^3$ . Two molecules of each type can be accommodated in the unit cell of the laths and this gives the correct cell volume and a calculated density of 3.27 g./c.c. The density could not be checked experimentally because of the lack of suitable suspension liquids. The presence of hexabromobenzene and tetrabromobenzene in the laths was confirmed by infrared spectroscopy: infrared spectra of the laths (KBr disc method, Infracord spectrometer) showed just the sum of the spectra of the two components (the occurrence of intensity changes and small frequency shifts was not investigated). Confirmation of the composition was given by the crystal-structure analysis described below.

*Crystal-Structure Analysis.*—The intensities of 300  $h0l$  (14 with  $I_{\text{obs}} = 0$ ) and 386  $h3l$  reflexions (77 with  $I_{\text{obs}} = 0$ ) were measured by the usual visual method from equi-inclination Weissenberg photographs about [010]. The intensities covered a range of about 10,000 to 1. Corrections were applied for Lorentz and polarization factors, spot shape<sup>11</sup> and absorption<sup>12</sup> (using the measured shape of the crystal). An approximate absolute scale was established by Wilson's<sup>13</sup> method.

The short [010] axis allows one to place the centres of the hexabromobenzene and tetrabromobenzene molecules respectively at point positions (a) (000,  $\frac{1}{2}\frac{1}{2}0$ ) and (b) ( $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ ,  $00\frac{1}{2}$ ) or (d) ( $\frac{1}{2}0\frac{1}{2}$ ,  $0\frac{1}{2}\frac{1}{2}$ ) of space group  $P2_1/a$ , (b) and (d) being of course indistinguishable in projection

<sup>8</sup> Herbstein, *Acta Cryst.*, 1958, **11**, 666.

<sup>9</sup> Glasstone, "Textbook of Physical Chemistry," Van Nostrand, New York, 1947, pp. 802–813.

<sup>10</sup> Gafner and Herbstein, *Acta Cryst.*, 1960, **13**, 702.

<sup>11</sup> Phillips, *Acta Cryst.*, 1954, **7**, 746; 1956, **9**, 819.

<sup>12</sup> Albrecht, *Rev. Sci. Inst.*, 1939, **10**, 221.

<sup>13</sup> Wilson, *Nature*, 1942, **150**, 152.

down [010]. The  $h0l$  Patterson projection was then computed and solved by considering, in the first instance, the intramolecular vector maps of the component molecules. Refinement by Fourier and least-squares methods led to acceptable bromine and carbon co-ordinates,  $R(h0l)$  being 16.5%. The  $v$ -coordinates of the atoms were then derived by calculating intermolecular non-bonded Br...Br distances for various models, it being assumed that the molecules were planar and regular, with  $d(\text{C-C}) = 1.40 \text{ \AA}$  and  $d(\text{C-Br}) = 1.90 \text{ \AA}$ . These calculations showed that the tetrabromobenzene molecules were at positions (d) and not (b) of the space group. These  $v$  co-ordinates, combined with  $u$  and  $w$  co-ordinates from the [010] projection, gave  $R(h3l) = 24\%$ .

The final refinement of the atomic parameters was done on an IBM 704 computer by using Busing and Levy's programme "OR XLS" to minimize  $\Sigma w|\Delta F|^2$ . The reflexions were weighted as follows.

$$\begin{aligned} w(hkl) &= (F_o/30)^2 \text{ for } |F_o| \leq 30 \\ &= (30/F_o)^2 \text{ for } |F_o| \geq 30 \\ &= (6/F_{\min})^2 \text{ when } I_{\text{obs}} = 0 \end{aligned}$$

This weighting scheme was adapted from that derived experimentally for  $\beta$ -1,2,4,5-tetrabromobenzene.<sup>14</sup> After some cycles of refinement with separate isotropic temperature factors for all atoms, anisotropic temperature factors were assigned to the bromines and further refinement carried out on all parameters except the isotropic temperature factors of the carbon atoms (the programme does not permit simultaneous refinement of isotropic and anisotropic temperature factors). Our experience with related compounds had convinced us that it was futile to attempt to assign anisotropic temperature factors to the carbon atoms. Hydrogen atoms were not included at any stage. The shifts indicated after the last cycle of refinement were less than 1% of their estimated standard deviations. The final values of  $R$  and  $R_2$   $\{ = [\Sigma w(F_o - F_c)^2 / \Sigma w F_o^2]^{1/2} \}$  were 13.8 and 14.3%, respectively. The quantity  $\{ \Sigma w(F_o - F_c)^2 / (m - n) \}^{1/2}$ , where  $m$  is the number of observations and  $n$  the number of variables, was 3.62 after the final cycle of refinement, indicating over-estimation of the absolute weights assigned to the reflexions.

The final atomic parameters are given in Table 1 and the values of observed and calculated structure factors in Table 2.

TABLE 1.

Atomic parameters and estimated standard deviations from final least-squares cycle.

(Temperature factor  $T = \exp - (h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})$  for bromine atoms.  
 $= \exp (-B \sin^2 \theta / \lambda^2)$  for carbon atoms (these values and their e.s.d.'s taken from last-refinement cycle with isotropic temperature factors).)

		Fractional co-ordinates			$B$						
Molecule	Atom	$u$	$v$	$w$	( $\text{\AA}^2$ )	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
$\text{C}_6\text{Br}_6$	Br 1	0.0942	0.1630	-0.1530		0.0025	0.0525	0.0048	-0.0028	0.0023	0.0002
		0.0002	0.0015	0.0003		0.0001	0.0091	0.0002	0.0007	0.0001	0.0009
	Br 2	0.1908	-0.1922	0.0628		0.0013	0.0444	0.0060	0.0010	0.0012	-0.0002
0.0002		0.0014	0.0003		0.0001	0.0091	0.0002	0.0006	0.0001	0.0009	
Br 3	0.0968	-0.3591	0.2144		0.0030	0.0291	0.0037	0.0029	0.0009	0.0032	
	0.0003	0.0012	0.0003		0.0002	0.0092	0.0002	0.0006	0.0001	0.0007	
C 1	0.0380	0.059	-0.0649	1.09							
	0.0015	0.009	0.0019	0.59							
C 2	0.0846	-0.114	0.0276	1.82							
	0.0018	0.010	0.0022	0.69							
C 3	0.0395	-0.142	0.0918	1.78							
	0.0018	0.011	0.0022	0.69							
sym.- $\text{C}_6\text{H}_2\text{Br}_4$	Br 4	0.1560	0.2220	0.4533		0.0021	0.0280	0.0056	0.0024	0.0021	0.0010
		0.0002	0.0012	0.0003		0.0001	0.0091	0.0003	0.0005	0.0001	0.0007
Br 5	0.1782	0.5524	0.6767		0.0019	0.0523	0.0041	-0.0023	0.0003	0.0001	
	0.0002	0.0015	0.0003		0.0001	0.0093	0.0002	0.0007	0.0001	0.0009	
C 4	0.0686	0.389	0.4831	2.01							
	0.0019	0.011	0.0022	0.76							
C 5	0.0787	0.529	0.5751	1.58							
	0.0018	0.010	0.0021	0.64							
C 6	0.0118	0.631	0.5967	1.76							
	0.0018	0.011	0.0021	0.69							

<sup>14</sup> Gafner and Herbstein, *Acta Cryst.*, 1960, **13**, 706.



TABLE 2. (Continued.)

$h$	$k$	$l$	$ F_o $	$F_c$	$h$	$k$	$l$	$ F_o $	$F_c$	$h$	$k$	$l$	$ F_o $	$F_c$	$h$	$k$	$l$	$ F_o $	$F_c$
3	3	4	40.8	39.9	11	3	0	33.7	-38.3	-4	3	10	27.2	-21.3	-10	3	12	3.5*	-2.6
3	3	5	29.3	-29.7	11	3	1	42.0	-48.2	-4	3	11	4.3*	-7.5	-10	3	13	18.7	17.6
3	3	6	32.0	-31.8	11	3	2	4.3*	-8.8	-4	3	12	3.5*	0.7	-10	3	14	17.6	-20.4
3	3	7	4.3*	-5.1	11	3	3	4.3*	-2.7	-4	3	13	42.6	33.9	-11	3	1	37.4	-24.8
3	3	8	40.8	-45.1	11	3	4	64.9	71.9	-4	3	14	35.6	-35.3	-11	3	2	35.6	-26.7
3	3	9	14.7	-11.5	11	3	5	43.7	34.3	-5	3	1	4.3*	-9.1	-11	3	3	52.4	-45.4
3	3	10	40.1	-41.5	11	3	6	23.9	-14.9	-5	3	2	22.2	18.1	-11	3	4	5.4*	-4.6
3	3	11	3.5*	-1.9	11	3	7	28.3	-22.3	-5	3	3	23.9	-14.6	-11	3	5	44.5	38.4
3	3	12	31.2	35.7	11	3	8	20.6	28.5	-5	3	4	110.5	-107.1	-11	3	6	59.5	-61.1
4	3	0	33.1	-30.4	12	3	0	14.9	-11.3	-5	3	5	46.4	40.7	-11	3	7	27.2	-16.5
4	3	1	35.6	58.9	12	3	1	4.3*	-11.1	-5	3	6	42.6	30.9	-11	3	8	4.3*	4.1
4	3	2	17.9	-7.2	12	3	2	42.0	-32.6	-5	3	7	130.9	130.9	-11	3	9	88.2	77.6
4	3	3	18.7	-26.0	12	3	3	23.9	19.5	-5	3	8	51.8	48.0	-11	3	10	68.7	67.4
4	3	4	42.6	55.1	12	3	4	35.6	-39.1	-5	3	9	39.1	-29.5	-11	3	11	39.1	35.9
4	3	5	4.3*	13.6	12	3	5	31.2	30.1	-5	3	10	50.8	-40.1	-11	3	12	31.2	-30.3
4	3	6	28.3	-33.5	12	3	6	23.9	23.9	-5	3	11	20.6	11.4	-11	3	13	29.3	-28.0
4	3	7	37.4	-40.5						-5	3	12	42.6	29.8	-11	3	14	14.9	18.8
4	3	8	19.7	27.4	13	3	0	18.7	12.2	-5	3	13	21.4	-19.6	-12	3	1	4.3*	5.3
4	3	9	29.3	-33.5	13	3	1	24.9	-19.1	-5	3	14	2.4*	-2.7	-12	3	2	66.8	51.6
4	3	10	4.3*	16.2	13	3	2	27.6	-16.4	-5	3	15	11.4	-18.7	-12	3	3	16.8	-15.3
4	3	11	12.4	-13.9	13	3	3	43.7	47.9	-6	3	1	45.1	-40.4	-12	3	4	62.4	-48.2
4	3	12	16.2	-15.1	13	3	4	11.4	10.4	-6	3	2	4.3*	11.7	-12	3	5	60.5	39.9
5	3	0	56.0	-60.5	13	3	5	2.4*	-7.2	-6	3	3	23.9	25.3	-12	3	6	44.5	-30.8
5	3	1	24.9	-22.6	13	3	6	12.4	-7.7	-6	3	4	54.3	-47.3	-12	3	7	32.0	26.2
5	3	2	4.3*	12.7	14	3	0	54.3	62.9	-6	3	5	54.3	40.9	-12	3	8	29.3	-35.2
5	3	3	45.1	-63.1	14	3	1	3.5*	1.8	-6	3	6	94.5	-92.1	-12	3	9	4.3*	4.1
5	3	4	4.3*	-13.3	14	3	2	3.5*	-3.5	-6	3	7	42.6	-24.1	-12	3	10	45.1	-50.1
5	3	5	25.8	-26.6	14	3	3	3.5*	-11.7	-6	3	8	40.1	-23.1	-12	3	11	42.6	45.2
5	3	6	40.1	48.5	14	3	4	35.6	36.1	-6	3	9	46.4	35.7	-12	3	12	3.5*	7.3
5	3	7	49.9	73.6						-6	3	10	59.5	-47.1	-12	3	13	2.4*	-6.7
5	3	8	32.0	39.4	15	3	0	3.5*	-12.5	-6	3	11	4.3*	5.5	-12	3	14	19.7	16.9
5	3	9	42.0	-46.1	15	3	1	25.8	-18.2	-6	3	12	3.5*	3.3	-13	3	1	100.7	96.5
5	3	10	14.9	-10.3	15	3	2	32.0	-37.6	-6	3	13	3.5*	-6.6	-13	3	2	46.4	30.2
5	3	11	28.3	23.0	15	3	3	14.9	-17.3	-6	3	14	30.1	-28.6	-13	3	3	27.6	19.8
5	3	12	24.9	16.6	16	3	0	2.4*	-8.5	-7	3	1	32.0	-19.5	-13	3	4	58.5	-44.5
6	3	0	33.1	-25.4	16	3	1	16.2	-19.5	-7	3	2	73.9	-86.5	-13	3	5	68.7	-55.8
6	3	1	48.0	-54.6	16	3	2	7.0	7.8	-7	3	3	12.4	-13.3	-13	3	6	5.4*	-10.8
6	3	2	43.7	-49.4						-7	3	4	4.3*	4.6	-13	3	7	29.3	-17.8
6	3	3	40.8	53.9	17	3	0	7.0	11.4	-7	3	5	61.4	-51.5	-13	3	8	21.4	-17.7
6	3	4	53.5	-75.7						-7	3	6	41.6	-27.5	-13	3	9	26.6	-23.2
6	3	5	21.4	30.7	-1	3	1	—	35.4	-7	3	7	4.3*	9.2	-13	3	10	36.6	33.9
6	3	6	23.9	-28.7	-1	3	2	43.7	-48.5	-7	3	8	4.3*	0.8	-13	3	11	38.3	-34.7
6	3	7	5.4*	9.5	-1	3	3	67.6	-74.0	-7	3	9	77.6	-54.2	-13	3	12	19.7	-12.7
6	3	8	5.4*	14.6	-1	3	4	23.9	14.5	-7	3	10	3.5*	0.5	-13	3	13	19.7	-17.3
6	3	9	40.8	36.3	-1	3	5	36.6	-34.2	-7	3	11	4.3*	-1.9	-14	3	1	22.2	27.8
6	3	10	24.9	-18.4	-1	3	6	30.1	-31.8	-7	3	12	72.8	66.5	-14	3	2	55.1	-49.2
6	3	11	10.6	-10.9	-1	3	7	67.6	-61.4	-7	3	13	48.9	44.8	-14	3	3	36.6	23.3
7	3	0	4.3	14.8	-1	3	8	26.6	17.3	-7	3	14	2.4*	-6.3	-14	3	4	24.9	9.7
7	3	1	93.4	112.9	-1	3	9	39.1	27.5	-7	3	15	22.2	-30.9	-14	3	5	4.3*	-1.8
7	3	2	74.7	86.9	-1	3	10	89.1	90.7	-8	3	1	86.4	94.2	-14	3	6	5.4*	1.6
7	3	3	36.4	43.6	-1	3	11	4.3*	-1.3	-8	3	2	53.5	-45.9	-14	3	7	49.9	33.6
7	3	4	64.9	-72.9	-1	3	12	47.0	-39.9	-8	3	3	21.4	17.0	-14	3	8	30.1	20.7
7	3	5	26.6	29.0	-1	3	13	2.5*	0.8	-8	3	4	46.4	45.0	-14	3	9	33.1	-29.2
7	3	6	37.4	37.4	-1	3	14	11.4	16.3	-8	3	5	39.1	31.4	-14	3	10	42.6	36.5
7	3	7	10.2	7.3	-2	3	1	85.3	102.6	-8	3	6	17.6	-15.8	-14	3	11	42.6	-15.7
7	3	8	5.4*	-10.4	-2	3	2	39.9	33.6	-8	3	7	4.3*	-3.0	-14	3	12	30.1	25.9
7	3	9	45.1	-32.0	-2	3	3	8.9	2.9	-8	3	8	4.3*	13.4	-15	3	1	3.5*	-11.0
7	3	10	21.4	-15.5	-2	3	4	46.4	37.7	-8	3	9	43.7	-36.0	-15	3	2	45.1	53.2
8	3	0	32.6	35.7	-2	3	5	30.1	-21.2	-8	3	10	51.8	43.3	-15	3	3	3.5*	-6.4
8	3	1	22.2	-24.2	-2	3	6	10.6	11.6	-8	3	11	48.0	-45.2	-15	3	4	25.8	-20.0
8	3	2	29.3	28.6	-2	3	7	4.3*	4.1	-8	3	12	35.6	-22.5	-15	3	5	30.1	-16.4
8	3	3	5.4*	9.4	-2	3	8	40.1	31.1	-8	3	13	23.9	-17.8	-15	3	6	85.3	69.5
8	3	4	31.2	29.8	-2	3	9	97.0	-93.2	-8	3	14	16.8	22.2	-15	3	7	57.8	42.8
8	3	5	44.5	-41.1	-2	3	10	4.3*	11.7	-9	3	1	84.7	-84.8	-15	3	8	60.5	45.9
8	3	6	5.4*	4.2	-2	3	11	17.9	-13.1	-9	3	2	5.4*	3.4	-15	3	9	24.9	-17.8
8	3	7	61.4	50.0						-9	3	3	98.8	114.9	-15	3	10	40.8	-39.6
8	3	8	32.0	-19.5	-3	3	1	64.9	81.1	-9	3	4	43.7	34.9	-16	3	1	42.6	-48.4
8	3	9	3.5*	4.1	-3	3	2	109.5	129.2	-9	3	5	55.1	52.0	-16	3	2	3.5*	-3.4
8	3	10	18.7	-11.9	-3	3	3	24.9	6.9	-9	3	6	13.3	11.2	-16	3	3	16.8	-11.8
9	3	0	52.4	48.6	-3	3	4	79.3	-70.2	-9	3	7	72.2	-60.1	-16	3	4	3.5*	12.2
9	3	1	37.4	36.4	-3	3	5	48.0	-43.4	-9	3	8	27.6	-20.9	-16	3	5	61.4	-64.2
9	3	2	19.7	-22.3	-3	3	6	50.8	35.1	-9	3	9	49.9	40.3	-16	3	6	25.8	20.9
9	3	3	20.6	-13.7	-3	3	7	28.3	10.6	-9	3	10	20.6	-14.9	-16	3	7	63.2	-52.6
9	3	4	48.0	-37.7	-3	3	8	54.3	-50.1	-9	3	11	4.3*	-4.3	-16	3	8	25.8	19.9
9	3	5	16.8	-16.0	-3	3	9	4.3*	-5.7	-9	3	12	21.4	-9.6	-16	3	9	25.8	17.9
9	3	6	55.1	-40.3	-3	3	10	37.4	-26.2	-9	3	13	3.5*	-0.3	-17	3	1	23.1	-24.0
9	3	7	4.3*	-14.1	-3	3	11	27.6	-18.6	-9	3	14	31.2	-28.5	-17	3	2	7.9	-18.7
9	3	8	36.6	-33.7	-3	3	12	45.1	-33.3	-10	3	1	38.3	-29.8	-17	3	3	26.6	-33.9
9	3	9	39.1	30.3	-3	3	13	16.8	-13.8	-10	3	2	4.3*	3.7	-17	3	4	18.7	-16.9
10	3	0	53.3	-50.7	-4	3	1	76.6	-104.7	-10	3	3	64.9	-50.5	-17	3	5	3.5*	-6.0
10	3	1	25.8	24.5	-4														

Interatomic distances and angles and their associated e.s.d.'s were calculated from the results of the last refinement cycle with Busing and Levy's programme "OR XFE." The e.s.d.'s cited include allowance for errors in cell dimensions. It is considered that the  $b_{ij}$  values for the bromine atoms are not accurate enough (because of the approximate nature of the absorption corrections for the very unsymmetrically-shaped crystals) to warrant any detailed discussion of the thermal motion. The best molecular planes for the two molecules were obtained by the method of Schomaker, Waser, Bergmann, and Marsh,<sup>15</sup> with bromine and carbon given relative weights of 50 and 1, respectively.

## DISCUSSION

*Molecular Arrangement.*—The molecular arrangement in projection down the three crystallographic axes is shown in Fig. 1, together with the shorter intermolecular distances.

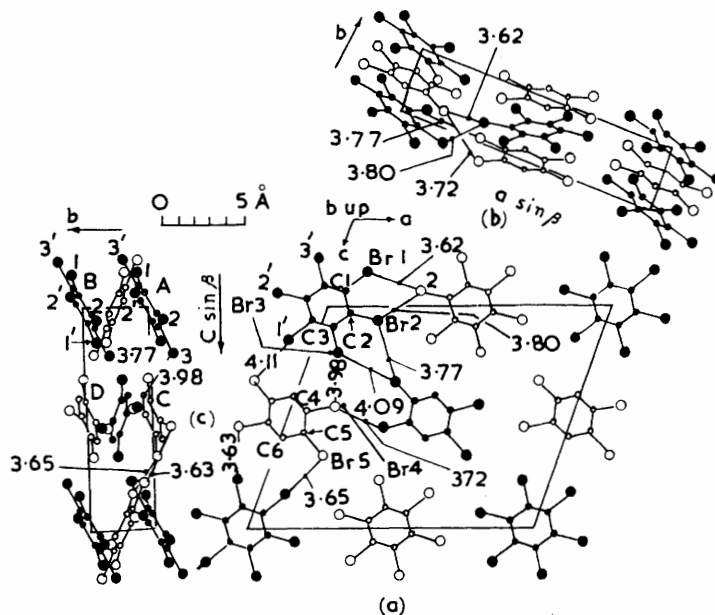


FIG. 1. Molecular arrangement and some shorter intermolecular distances (approximate e.s.d.'s are: Br...Br, 0.01; Br...C, 0.03; C...C, 0.04 Å). Many symmetry-related distances have not been included. Projections of unit-cell contents down (a) [010], (b) [001], (c) [100] are shown. Molecules whose centres lie in the plane of the paper are drawn with filled circles, those above or below the plane of the paper by half the appropriate unit-cell translation have open circles. The shorter intermolecular distances within stacks are:

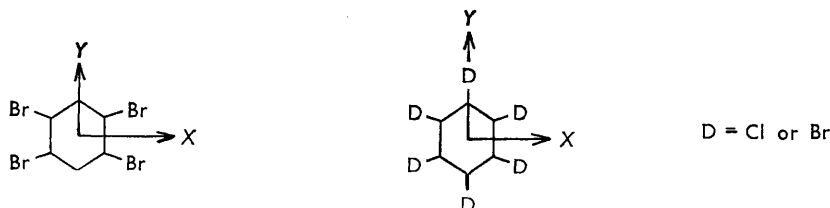
Stack of $C_6Br_6$ molecules			Stack of sym.- $C_6H_2Br_4$ molecules		
A	B		C	D	
Br 1	Br 1	4.01 Å	Br 4	Br 4	4.01 Å
(and similarly for other symmetry-related distances)					
Br 1	Br 2	3.94	Br 5	Br 4	4.10
	C 2	3.94	C 4	Br 4	3.77
Br 3'	C 1	3.82	C 5	Br 4	3.80
	C 3	3.57		C 4	3.68
C 1	C 2	3.56	C 6	C 4	3.76
	C 3	3.91			
C 1'	C 3	3.90			
C 2'	C 3	3.74			
C 3'	C 3	3.81			

<sup>15</sup> Schomaker, Waser, Bergmann, and Marsh, *Acta Cryst.*, 1959, **12**, 600.

The molecules are arranged in stacks whose axes are parallel to  $[010]$ , any one stack containing molecules of one kind only. Each stack is surrounded by six nearest-neighbour stacks in a quasi-hexagonal array; of these six neighbouring stacks, two contain the same type of molecule as the central stack, while four contain the second component. The interplanar spacing in the tetrabromobenzene stack is  $3.63 \text{ \AA}$ , identical with that in  $\beta$ -1,2,4,5-tetrabromobenzene<sup>14</sup> and the relative arrangement of molecules separated by unit translation along  $[010]$  (Fig. 2) is very similar to that in the  $\beta$ -polymorph.

TABLE 3.

Co-ordinates of centre of molecule moved unit translation up stack in terms of orthogonal molecular axes  $X, Y, Z$  (see diagrams for definition). Note that the interplanar spacing is given by the value of  $Z$ .



Molecule	Crystal	Co-ordinates of centre in $\text{\AA}$			Reference
		$X$	$Y$	$Z$	
Tetrabromobenzene	$\beta$ -Phase	0.51 <sub>6</sub>	-1.62 <sub>5</sub>	3.63 <sub>0</sub>	14
	$\gamma$ -Phase	0.92	-1.45	3.69	16a
Hexabromobenzene	Molecular complex	-0.64	-1.58	3.63	Present Paper
Hexachlorobenzene	Hexachlorobenzene	-1.56	0.81	3.61	Present Paper
		-0.86	1.18	3.58	16

This is also shown in Table 3 where the co-ordinates of the centre of the molecule moved unit translation along  $[010]$  are given in terms of the molecular axes  $X, Y, Z$ . In the hexabromobenzene stack the interplanar spacing is  $3.61 \text{ \AA}$  (comparable value for hexabromobenzene itself not available). The relative arrangement of superimposed molecules in a stack is shown in Fig. 3a, while that in hexachlorobenzene<sup>16</sup> is shown in Fig. 3b. The co-ordinates of the molecular centres in terms of the molecular axes are given in Table 3.

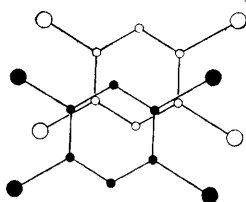


FIG. 2.

FIG. 2. Normal projection of two tetrabromobenzene molecules in the same stack separated by unit translation along  $[010]$ .

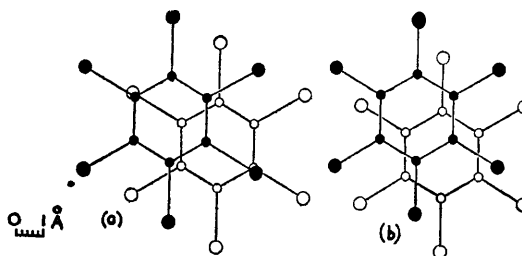


FIG. 3.

FIG. 3. Normal projection of two molecules in the same stack separated by unit translation along  $[010]$ .

- (a) hexabromobenzene molecules (in molecular complex with tetrabromobenzene). Br 1 at top of diagram;  
 (b) hexachlorobenzene molecules (in hexachlorobenzene). Cl 1 at top of diagram.

The molecular arrangement in the complex resembles the arrangement in hexabromobenzene (unknown in detail at present but presumed similar to that in the isomorphous

<sup>14</sup> Strel'tsova and Struchkov, *J. Struct. Chem.*, 1961, 2, 296.

<sup>16a</sup> Grafner and Herbstein, *Acta Cryst.*, 1964, 17, 982.

hexachlorobenzene) much more closely than that in tetrabromobenzene. From a formal point of view one can distinguish sheets of hexabromobenzene molecules in the complex parallel to (001) which are similar to the sheets of hexabromobenzene molecules parallel to (101) in hexabromobenzene itself (cf. Fig. 6). However, the distances between stacks of like and unlike molecules in the complex are very similar and there is no evidence for stronger bonding within the sheets than between them. Thus, from a physical point of view, descriptions of the molecular packing in terms of stacks or sheets appear to be equally valid. The intermolecular distances are such that only van der Waals interactions are indicated.

*Comparison with Similar Structures.*—The segregated stacks found in the present molecular complex appear to be typical of the molecular arrangements in binary crystals where only van der Waals intermolecular interactions occur. Similar segregated stacks are found in molecular complexes where the components are geometrical isomers (*e.g.*, octamethylcyclotetrasilazane<sup>17</sup> (Me<sub>2</sub>SiNH)<sub>4</sub>) and optical enantiomorphs (*e.g.*, 9,10-dimethylbenz[*a*]anthracene<sup>18</sup>). On the other hand, the polarization-bonded molecular compounds formed between electron donors (*e.g.*, aromatic hydrocarbons) and various electron acceptors (*e.g.*, 1,3,5-trinitrobenzene) all have mixed stacks, *i.e.*, both components are present in any one stack, one above the other in regular alternation. One deduces from the relatively short interplanar distances that there is some type of special bonding between the components. Typical crystal structures have been reported by Powell and his co-workers,<sup>19</sup> Wallwork,<sup>3a</sup> de Santis *et al.*<sup>20</sup> and Hanson.<sup>21</sup>

There is one other molecular complex which can be usefully compared with hexabromobenzene-tetrabromobenzene. This is XeF<sub>2</sub>.XeF<sub>4</sub><sup>22</sup> ( $a = 6.40$ ,  $b = 7.33$ ,  $c = 6.64$  Å,  $\beta = 92^\circ 40'$ , space group  $P2_1/a$ , 2 molecules each of XeF<sub>2</sub> and XeF<sub>4</sub> in the unit cell; the  $a$  and  $c$  axes in ref. 22 have been interchanged to facilitate comparison with the present results). Burns *et al.*<sup>22</sup> state that "there is no structural evidence for the formation of any strong bonds between molecules and this phase appears to be appropriately described as a molecular addition compound." In a formal sense the structures of the two complexes are identical: the space groups are the same, the centrosymmetric molecules are distributed over the same special positions of the space group, and the structure can be described in terms of face-centred sheets parallel to (001), alternate sheets containing one kind of molecule only. This is the same as one of the descriptions given for hexabromobenzene-tetrabromobenzene. There is another point of resemblance in that the molecular arrangement in XeF<sub>2</sub>.XeF<sub>4</sub> is rather similar to that in XeF<sub>4</sub><sup>23</sup> but not at all to that in XeF<sub>2</sub>.<sup>24</sup> The crystallographic parameters for XeF<sub>4</sub> are  $a' = 6.95$ ,  $b' = 5.924$ ,  $c' = 5.058$  Å,  $\beta' = 117.1^\circ$ , space group  $P2_1/a$ ; these axes, chosen for convenience in the present discussion, are related to those used previously by  $\mathbf{a}' = \mathbf{a} + \mathbf{c}$ ,  $\mathbf{b}' = \mathbf{b}$ ,  $\mathbf{c}' = -\mathbf{a}$ , original  $\beta = 99.6^\circ$  and original space group  $P2_1/a$ . In XeF<sub>4</sub> itself the molecules in the (001) faces are in a face-centred arrangement but the dimensions of the sheets differ somewhat in XeF<sub>4</sub> and XeF<sub>2</sub>.XeF<sub>4</sub>. XeF<sub>2</sub> has a body-centred tetragonal structure which bears no resemblance to that of XeF<sub>4</sub> or XeF<sub>2</sub>.XeF<sub>4</sub>.

Some information about the intermolecular bonding in these complexes can be obtained from a comparison of their densities with those in the components (Table 4; calculated values have been used as experimental values are not available). The density of hexabromobenzene-tetrabromobenzene is not significantly different from the mean of the

<sup>17</sup> Smith and Alexander, *Acta Cryst.*, 1963, **16**, 1015.

<sup>18</sup> Sayre and Friedlander, *Nature*, 1960, **187**, 139.

<sup>19</sup> (a) Powell, Huse, and Cooke, *J.*, 1943, 153; (b) Powell and Huse, *J.*, 1943, 435.

<sup>20</sup> De Santis, Giglio, Liquori, and Ripamonti, *Nature*, 1961, **191**, 900.

<sup>21</sup> Hanson, *Acta Cryst.*, 1963, **16**, 1147.

<sup>22</sup> Burns, Ellison, and Levy, *J. Phys. Chem.*, 1963, **67**, 1569.

<sup>23</sup> (a) Templeton, Zalkin, Forester, and Williamson, *J. Amer. Chem. Soc.*, 1963, **85**, 242; (b) Burns, Agron, and Levy, *Science*, 1963, **139**, 1208.

<sup>24</sup> (a) Siegel and Gebert, *J. Amer. Chem. Soc.*, 1963, **85**, 240; (b) Levy and Agron, *ibid.*, 1963, **85**, 241.



TABLE 4.

Calculated densities of the molecular complexes and their components. The references give the sources of the cell dimensions from which these values were calculated.

Components of complex	Calculated density (g./c.c.)	Mean of component densities (g./c.c.)	Calculated density of complex (g./c.c.)
Hexabromobenzene .....	3.554 <sup>20</sup>	} 3.277	3.27 <sub>0</sub> *
1,2,4,5-Tetrabromobenzene .....	3.020 <sup>14</sup>		
XeF <sub>4</sub> .....	4.044 <sup>23a</sup>	} 4.181	4.018 <sup>22</sup>
XeF <sub>2</sub> .....	4.318 <sup>24a</sup>		

\* This Paper.

component densities, suggesting that the intermolecular bonding is similar in the complex and in the individual components. The density of XeF<sub>4</sub>,XeF<sub>2</sub> is even lower than that of XeF<sub>4</sub>, despite replacement of half the XeF<sub>4</sub> molecules with denser XeF<sub>2</sub> molecules. Discussion of the intermolecular bonding in the xenon fluorides is complicated by the fact that Xe...F interactions seem also to be important (the shortest Xe...F distances are 3.42 Å in XeF<sub>2</sub>, 3.22 and 3.25 Å in XeF<sub>4</sub>, and 3.28, 3.35, 3.35, 3.37, and 3.42 Å in XeF<sub>2</sub>,XeF<sub>4</sub>, compared to van der Waals radii of 2.17 Å for Xe (from the element)<sup>25</sup> and 1.35—1.50 Å for F). Judging from the molecular arrangement, intermolecular distances, and density, the intermolecular bonding seems to be similar in XeF<sub>4</sub> and XeF<sub>2</sub>,XeF<sub>4</sub>. The density of crystalline XeF<sub>2</sub> appears to be anomalously high and this is probably a consequence of the compact packing possible with quasi-cylindrical molecules and not of stronger intermolecular bonding; the intermolecular distances in XeF<sub>2</sub> are in fact slightly longer than those in XeF<sub>4</sub>. In XeF<sub>2</sub>,XeF<sub>4</sub> the shorter Xe...F and F...F distances are in the XeF<sub>4</sub> sheets and between the two types of sheet; within the XeF<sub>2</sub> sheet there is only a fairly close approach between Xe and F (3.42 Å). Thus there appears to be little difference between the density of packing of hexabromobenzene and tetrabromobenzene molecules in the molecular complex or in the individual components, whereas XeF<sub>2</sub> molecules are packed appreciably more compactly in XeF<sub>2</sub> crystals than in XeF<sub>2</sub>,XeF<sub>4</sub>.

*Molecular Dimensions.*—The molecular planes through the atoms of each molecule are referred to orthogonal axes  $x'$ ||[100],  $y'$ ||[010], and  $z'$  along the normal to (001) (lengths measured in Å). The equations of the molecular planes were calculated by assuming the molecular centres of symmetry to lie at the origin of the co-ordinate system in both cases.

$$\text{hexabromobenzene: } 0.1118 x' + 0.8994 y' + 0.4225 z' = 0$$

$$\text{1,2,4,5-tetrabromobenzene: } 0.2651 x' + 0.9053 y' - 0.3320 z' = 0$$

The dimensions given in Figs. 4a and 4b were calculated without making any allowance for thermal motion of the atoms; insufficient information is available for this to be done. The dimensions of the 1,2,4,5-tetrabromobenzene molecule are compatible with, but less accurate than, results obtained here from an analysis of  $\beta$ -1,2,4,5-tetrabromobenzene.<sup>14</sup> The molecular dimensions of hexabromobenzene are close to the values expected, only the bromine positions being accurate enough to warrant detailed discussion. The deviations of the atoms from the best molecular plane (see caption to Fig. 4b for details) are not significant. The three independent values of  $d(\text{Br}\cdots\text{Br})$  do not differ significantly from their weighted mean of  $3.279 \pm 0.008$  Å, which is also not significantly different from the mean distance ( $3.281 \pm 0.002$  Å) between bromine atoms and molecular centre. Thus the bromine atoms are arranged with symmetry  $D_{6h} - 6/mmm$ , and their positions are not affected by the lower symmetry ( $C_i - \bar{1}$ ) of the crystal field. The mean value of  $d(\text{Br}\cdots\text{Br})$  is very significantly different ( $\Delta l/\sigma \sim 10$ ) from that found in 1,2,4,5-tetrabromobenzene<sup>14</sup> ( $3.377 \pm 0.004$  Å), the reason being that buttressing prevents

<sup>25</sup> Sears and Klug, *J. Chem. Phys.*, 1962, **37**, 3002.

in-plane splaying apart of adjacent bromine atoms in hexabromobenzene but not in tetrabromobenzene.

The planarity of the two molecules and the in-plane splaying apart of the bromine atoms in 1,2,4,5-tetrabromobenzene agree qualitatively with the theoretical calculations of Coulson and Stocker.<sup>26</sup>

*Phase Relations.*—Some exploratory work has been done on the phase relations in the system: hexabromobenzene–1,2,4,5-tetrabromobenzene. The thermal decomposition studies described in the next section make it clear that at room temperature unconfined

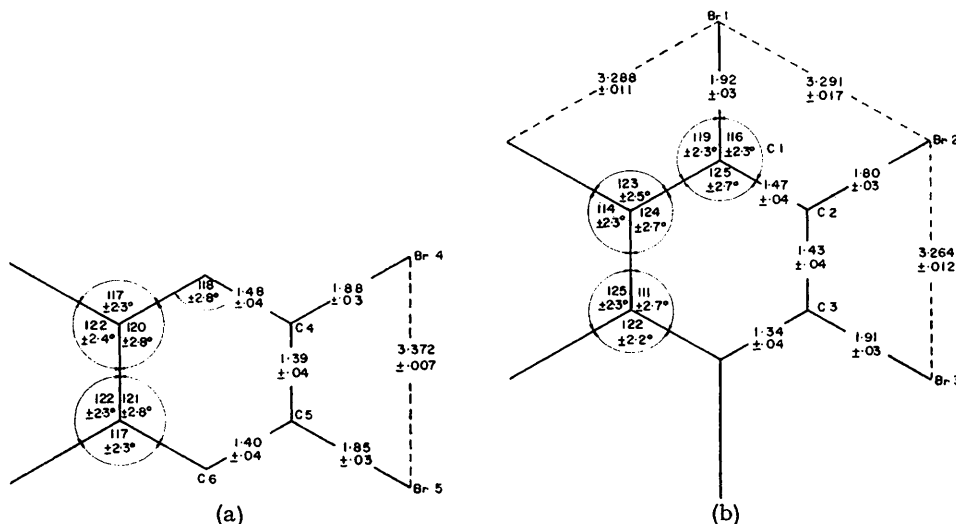
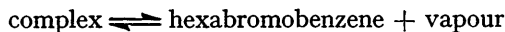


FIG. 4. (a) Dimensions for 1,2,4,5-tetrabromobenzene in molecular complex. Deviations from best molecular plane are: Br 4:  $-0.000_5$  Å; Br 5:  $-0.000_0$ ; C 4:  $+0.02$ ; C 5:  $+0.04$ ; C 6:  $-0.03$ .  
(b) Dimensions for hexabromobenzene in molecular complex. Deviations from best molecular plane are: Br 1:  $-0.006$  Å; Br 2:  $+0.007$ ; Br 3:  $-0.007$ ; C 1:  $-0.04$ ; C 2:  $-0.10$ ; C 3:  $+0.03$ .

(Note: A positive deviation means that the atom in question is on the 0,1,0 side of the plane.)

crystals of the molecular complex decompose to solid hexabromobenzene and vapour (mainly, but not necessarily entirely, tetrabromobenzene). Using this result and applying the phase rule, one concludes that the system



is univariant, with a definite dissociation pressure that varies with temperature. A discussion of this situation has been given by Glasstone.<sup>27</sup>

In another set of experiments the form of the liquidus was determined (Fig. 5) in an ordinary melting-point apparatus. The samples were contained in sealed tubes in order to minimize concentration changes due to differential evaporation of the components. Thus one investigates a variable-pressure section through the  $P$ - $T$ - $c$  space model, although the range of pressures is too small to affect the shape of the liquidus within the limited accuracy of the present measurements. There was no evidence for the formation of molecular complex in these experiments, *i.e.*, at temperatures above 150°. The results of both sets of experiments are compatible with Ricci's<sup>28</sup> detailed formal discussion of

<sup>26</sup> Coulson and Stocker, *Mol. Phys.*, 1959, 2, 397.

<sup>27</sup> Reference 9, pp. 778–786, 847–848.

<sup>28</sup> Ricci, "The Phase Rule and Heterogeneous Equilibrium," Van Nostrand, New York, 1951, pp. 126–132.

systems containing binary compounds with incongruent transitions. We do not plan a more quantitative study of this system.

The phase diagrams of 1,3,5-trinitrobenzene with a number of electron-donors have been determined;<sup>29</sup> the equimolar compounds show congruent melting points. This indicates that their stability is greater than that of the molecular compound with van der Waals bonds investigated here.

*Thermal Decomposition.*—Crystals of the complex were stable in contact with mother-liquor but after some days exposure to the atmosphere at room temperature initially transparent crystals became cloudy. When the solid molecular complex was heated on a microscope hot-stage, cracks were observed to appear in the crystals at about 130°, at which temperature tetrabromobenzene crystals heated under identical conditions begin to evaporate rapidly. At 150° the crystals of the complex were cloudy and ceased to show extinction; unfortunately they evaporated too rapidly for their melting point to be measured.

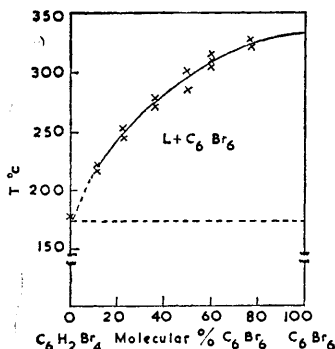


FIG. 5. Melting-point diagram for system hexabromobenzene-1,2,4,5-tetrabromobenzene. Dashed portions of diagram are schematic only and were not observed directly.

A preliminary study of the thermal decomposition of the molecular complex at room temperature was made by taking Weissenberg and oscillation photographs ( $\text{Cu-K}\alpha$  radiation) of a single crystal over a period of about one month. The crystal was mounted in the ordinary way and not protected from the atmosphere; room temperature varied from about 20 to 28°. After 10 days (when the second set of photographs was taken) powder lines of hexabromobenzene were observed as well as some rather diffuse single-crystal reflexions. After 22 days the powder lines were still present while the single-crystal hexabromobenzene reflexions had sharpened, although the  $\alpha_1\alpha_2$  doublet was still poorly resolved at high angles. Later the diffraction pattern of the complex became weaker but not less sharp; no powder lines of the complex were observed at any stage of the decomposition.

Only part of the hexabromobenzene formed as decomposition product was oriented with respect to the parent lattice. The orientation relationship found was

$$\begin{aligned} [010]_{\text{complex}} &\parallel [010]_{\text{C}_6\text{Br}_6} \\ (001)_{\text{complex}} &\parallel (101)_{\text{C}_6\text{Br}_6} \end{aligned}$$

This orientation relationship is referred to the unit cell of hexabromobenzene given by  $a = 15.382$ ,  $b = 4.002$ ,  $c = 8.377$  Å,  $\beta = 92.69^\circ$ .<sup>10,30</sup> It should be noted that the requirements that the three axes form a right-handed set and that  $\beta > 90^\circ$  enable one to define the  $+\mathbf{b}$  direction unequivocally from Weissenberg photographs; the common  $+\mathbf{b}$  direction of parent and product crystals is established without ambiguity. The orientation relationship between parent and product is shown in Fig. 6 and the close similarity

<sup>29</sup> Kofler, *Z. Elektrochem.*, 1944, **50**, 200.

<sup>30</sup> Herbstein, *Acta Cryst.*, 1963, **16**, 255.

between the arrangement of hexabromobenzene stacks along parallel planes in both crystals is evident. The repeat distances are also very similar:

$$[010]_{\text{complex}} \approx [010]_{\text{C}_6\text{Br}_6} \approx 4.01 \text{ \AA}$$

$$[100]_{\text{complex}} = 17.80 \text{ \AA}; [101]_{\text{C}_6\text{Br}_6} = 17.86 \text{ \AA}$$

These observations allow one to describe the thermal decomposition in general terms. The first stage is the loss of tetrabromobenzene from the surface of the crystal of the complex, leading to the appearance of polycrystalline product. However, tetrabromobenzene also diffuses out from the interior and the remaining hexabromobenzene molecules form small crystals of hexabromobenzene by a nucleation and growth process. There

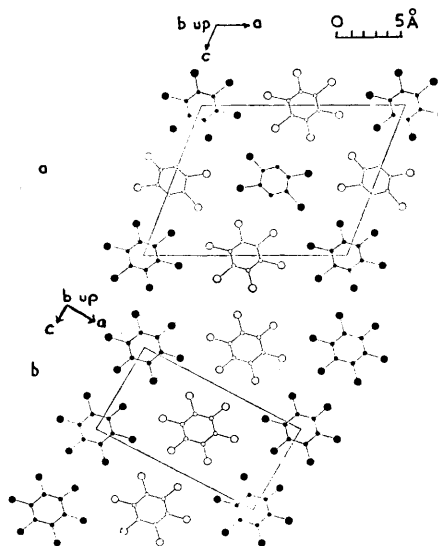


FIG. 6. The orientation relation is shown between the molecular complex (a) and the hexabromobenzene, (b) resulting from its thermal decomposition. Both crystals are illustrated in projection down [010]. Open and full circles have the same significance as in Fig. 1.

is a close orientation relationship between parent and product crystals which is presumably determined by the requirement of minimum interfacial energy.

The thermal decomposition described above is a topotactic reaction, according to the definition given by Dent Glasser, Glasser, and Taylor.<sup>5</sup> "In topotaxy," they claim, "a single crystal of a starting material is converted into a pseudomorph containing one or more products in a definite crystallographic orientation; the conversion takes place throughout the entire volume of the crystal. For true topotaxy there must be some three-dimensional correspondence between the structures of the product and its host . . . ." If one ignores the surface disorientation then this is an exact description of the decomposition of the molecular complex. Many inorganic topotactic reactions have been discussed.<sup>5</sup> A further topotactic reaction studied recently<sup>31</sup> is the decomposition of ammonium chlorite to ammonium chloride and ammonium chlorate. Close counterparts in organic chemistry are not known to us but some related reactions have been cited.<sup>6</sup>

Polarization-bonded molecular compounds also decompose thermally: for example pyromellitic dianhydride-benzene (1:1) loses benzene immediately on exposure to the atmosphere, leaving behind a pseudomorph of powdered pyromellitic dianhydride with very little, if any, preferred orientation.<sup>32</sup> Similar results have been reported for the molecular compound formed between hexamethylbenzene and picryl chloride.<sup>33</sup> The absence of topotactic reaction is presumably a consequence of the lack of close relationship

<sup>31</sup> Gillespie, Sparks, and Trueblood, *Acta Cryst.*, 1959, **12**, 867.

<sup>32</sup> Boeyens and Herbstein, unpublished results.

<sup>33</sup> Nitta, Seki, Chihara, and Suzuki, *Sci. Papers Osaka Univ.*, 1951, No. 29.

between the crystal structure of the molecular compound and that of the solid component which remains after decomposition, and this in turn is clearly related to the presence of mixed stacks in the polarization-bonded molecular compound.

We are grateful to the Dow Chemical Company for a gift of hexabromobenzene and to Drs. P. C. Carman and R. R. Arndt (both of the National Chemical Research Laboratory, Pretoria) for helpful discussions and the infrared spectra, respectively.

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[Received, January 9th, 1964.]

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