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The Crystal and Molecular Structures of Overcrowded Halogenated Compounds. V. γ-1,2:4,5-Tetrabromobenzene

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The crystal structure of γ-1,2:4,5-tetrabromobenzene (stable above 46 °C) has been determined by three-dimensional least-squares methods. The molecular conformation is the same as that in the β phase (stable below 46 °C) and the molecular arrangements in the two phases are very similar.

Introduction

The occurrence of a phase change in 1,2:4,5-tetrabromobenzene above room temperature was observed by Schaum, Schaeling & Klausing (1916) by microscopic methods. The temperature of the phase change was determined to be $46{\cdot}5 \pm 0{\cdot}2$ °C by measurements of the frequency of nuclear quadrupole resonance absorption (^{81}Br) (Johnson, 1956). We have reported preliminary crystallographic results for the γ phase stable above 46·5 °C (Gafner & Herbstein, 1960*a*, *c*). In the present paper the results of a three-dimensional analysis of the crystal structure of this phase are reported.

Crystal structure analysis

Crystallographic data

A crystal of the β phase (stable at room temperature) was inserted in a Lindemann-glass capillary and held securely with a coating of glue. This prevented shattering of the crystal when it was heated above the transformation temperature by blowing hot air over it (*cf.* Kreuger, 1955). The cell dimensions were measured from oscillation and front-reflexion Weissenberg photographs, the crystal temperature being 59 °C. The values* found were:

$$a = 10{\cdot}00 \pm 0{\cdot}01,\ b = 11{\cdot}18 \pm 0{\cdot}01,\ c = 4{\cdot}07 \pm 0{\cdot}02\ \text{Å};$$
$$\beta = 103^\circ\ 48' \pm 20'.$$

Density not measured; calculated value 2·957 g.cm^{-3}. Systematic absences showed the space group to be $P2_1/a$.

All γ-phase crystals examined, whether grown from the melt or by heating β-phase crystals, were found to be twinned on the (110) faces. This type of twinning is found in the β phase and has already been discussed in some detail (Gafner & Herbstein, 1960*b*).

Intensity measurements

The intensities of 571 *hk*0, *hk*1 and *hk*2 reflexions (of which 94 had $I_o = 0$) were measured with Cu $K\alpha$ (Ni filter) radiation on an equi-inclination Weissenberg camera, the standard multiple-film technique being used. The crystal temperature was 69 ± 5 °C. The first measurements were made on a β crystal that had been heated up from room temperature. The spot shape was not very satisfactory and another crystal was prepared in a capillary by cooling molten tetrabromobenzene. Results were somewhat better from the second crystal and these intensities were used in the analysis that follows. The intensities covered a range of about 1000:1. The usual correction factors (Lorentz, polarization, spot-shape, absorption (as for cylindrical crystal)) were applied and the absolute scale determined by Wilson's method. The photographs were not of high quality as the spot shape was poor and satellites (usually in twin orientation) accompanied the main crystal.

After these measurements at higher temperature had been completed it was found that γ-phase crystals held in a capillary do not transform to the β phase on cooling. Similar hysteresis has been noted by Johnson (1956).

Determination of atomic parameters

The structures of the β and γ phases are obviously closely related and similar methods were used in both structure determinations. Initial values of coordinates in the γ phase were derived from *hk*0 and *hk*1 Patterson syntheses and refined by least squares on the IBM 704 with Busing & Levy's program ORXLS (for details of atomic scattering factors and weights see Gafner & Herbstein, 1960*b*). Anisotropic temperature factors were used for the bromine atoms while the carbon atoms had separate, isotropic, temperature factors. Hydrogen atoms were not included. Refinement was continued until the largest parameter shifts were less than 30% of their standard deviations. The final R index (all reflections) is 12·6% while R_2 is 15·0%. Observed and calculated structure factors are listed in Table 1. Final atomic parameters and their standard deviations are given in Table 2.

Interatomic distances and angles and thermal-

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* The values given previously (Gafner & Herbstein, 1960*a*) were found later to be wrong.

Table 1. *Observed and calculated structure factors*

* $|F_o|$ low for these reflexions because of extinction. Dash in $|F_o|$ column indicates a reflexion that was not recorded. Dash for 020 inadvertently omitted.

$\times$ indicates a reflexion with $I_o=0$. $|F_o|=\frac{1}{2}F_{\min}$ for these reflexions.

h	k	ℓ	$\lvert F_o \rvert$	F_c
2	0	0	26.8	-23.0
4	0	0	52.3	-51.6
6	0	0	31.1	-32.7
8	0	0	37.3	-35.8
10	0	0	39.2	44.2
12	0	0	6.4	-8.0
1	1	0	-	-10.9
2	1	0	69.1	-79.0
3	1	0	80.8	81.4
4	1	0	86.1	-93.2
5	1	0	64.0	-68.2
6	1	0	38.3	43.7
7	1	0	36.4	39.4
8	1	0	21.5	20.4
9	1	0	7.7	-6.8
10	1	0	5.1$^{\times}$	1.0
11	1	0	12.4	-14.5
0	2	0		-1.9
1	2	0	55.5	-59.3
2	2	0	75.3	-91.0
3	2	0	77.6	72.5
4	2	0	55.9	56.1
5	2	0	4.1$^{\times}$	6.9
6	2	0	60.4	60.0
7	2	0	44.3	-43.5
8	2	0	23.9	-23.9
9	2	0	11.3	8.7
10	2	0	5.0$^{\times}$	1.3
11	2	0	13.5	-15.7
12	2	0	10.7	-14.3
1	3	0	33.0	33.6
2	3	0	127.6	134.3
3	3	0	3.5$^{\times}$	3.0
4	3	0	26.6	-25.8
5	3	0	56.2	-61.7
6	3	0	30.5	28.7
7	3	0	5.4$^{\times}$	2.8
8	3	0	54.9	-50.6
9	3	0	7.5	10.3
10	3	0	12.0	-13.1
11	3	0	5.8$^{\times}$	3.0
12	3	0	11.7	15.7
0	4	0	53.6	53.3
1	4	0	104.4	-123.0
2	4	0	18.8	12.8
3	4	0	10.0	-7.3
4	4	0	48.5	-50.2
5	4	0	4.5$^{\times}$	3.0
6	4	0	31.5	-27.7
7	4	0	6.6$^{\times}$	- 7.1
8	4	0	18.5	10.7
9	4	0	40.6	36.5
10	4	0	13.5	12.5
11	4	0	18.8	-19.3
1	5	0	54.3	-55.9
2	5	0	10.0	-4.8
3	5	0	28.7	-24.3
4	5	0	71.5	-68.8
5	5	0	62.1	64.2
6	5	0	59.3	57.7
7	5	0	8.1	7.9
8	5	0	5.4$^{\times}$	4.8
9	5	0	5.1$^{\times}$	-1.8
10	5	0	4.5$^{\times}$	-4.0
11	5	0	6.7	-6.7
0	6	0	94.9	-87.3
1	6	0	4.1$^{\times}$	-7.8
2	6	0	25.6	23.5
3	6	0	72.1	70.7
4	6	0	7.1$^{\times}$	6.8
5	6	0	23.2	20.3
6	6	0	5.2$^{\times}$	6.9
7	6	0	33.9	-29.9
8	6	0	20.5	18.7
9	6	0	4.7$^{\times}$	1.3
10	6	0	20.3	-20.1
1	7	0	62.1	65.0
2	7	0	21.5	15.8
3	7	0	48.7	-46.1
4	7	0	7.1$^{\times}$	-4.7
5	7	0	5.4$^{\times}$	1.6
6	7	0	8.1	8.9
7	7	0	33.9	-30.7
8	7	0	5.0$^{\times}$	-2.7
9	7	0	12.8	12.2
0	8	0	33.9	-32.5
1	8	0	31.7	-28.7
2	8	0	31.5	35.8
3	8	0	51.9	-53.2
4	8	0	11.1	-9.8
5	8	0	5.2$^{\times}$	-2.3
6	8	0	13.2	-10.3
7	8	0	26.6	24.1
8	8	0	22.2	18.8
9	8	0	11.5	9.6
10	8	0	13.0	-12.7
1	9	0	20.2	-18.4
2	9	0	13.0	-16.5
3	9	0	10.5	-10.7
4	9	0	10.7	11.9
5	9	0	43.2	48.0
6	9	0	10.0	-7.6
7	9	0	4.7$^{\times}$	-2.7
8	9	0	4.1$^{\times}$	3.3
9	9	0	9.2	-7.6
0	10	0	5.4$^{\times}$	-3.0
1	10	0	31.5	31.8
2	10	0	20.9	17.6
3	10	0	13.2	7.9
4	10	0	7.5	-5.5
5	10	0	5.0$^{\times}$	0.1
6	10	0	13.5	-12.4
7	10	0	8.6	-6.0
1	11	0	20.0	19.9
2	11	0	20.9	-26.6
3	11	0	10.0	-9.0
4	11	0	7.1$^{\times}$	4.6
5	11	0	14.5	-14.3
6	11	0	8.1	-10.3
7	11	0	6.7	-7.8
0	12	0	9.8	-12.5
1	12	0	6.8$^{\times}$	2.3
2	12	0	6.6$^{\times}$	-9.1
3	12	0	20.3	-22.2
4	12	0	8.6	6.8
1	13	0	10.0	-12.9
2	13	0	3.7$^{\times}$	4.8
3	13	0	3.5$^{\times}$	7.0
4	13	0	13.5	16.6
0	14	0	9.0	14.6
1	14	0	5.8	7.8
10	0	1	12.9	-13.4
8	0	1	45.9	49.3
6	0	1	48.3	-48.0
4	0	1	90.1*	-107.9
2	0	1	61.1	74.9
0	0	1	-	19.7
-2	0	1	-	195.9
-4	0	1	26.8	-28.2
-6	0	1	65.8*	-90.4
-8	0	1	17.8	20.3
-10	0	1	10.1	-10.4
9	1	1	10.5	3.8
8	1	1	32.8	32.4
7	1	1	32.0	-32.7
6	1	1	7.3	7.2
5	1	1	68.6	74.8
4	1	1	3.1$^{\times}$	0.9
3	1	1	62.4	-68.9
2	1	1	89.4*	-115.6
1	1	1	13.1	11.4
0	1	1	-	-45.3
-1	1	1	-	64.4
-2	1	1	93.3	104.9
-3	1	1	69.7	-52.9
-4	1	1	43.8	41.7
-5	1	1	53.6	67.7
-6	1	1	19.6	19.4
-7	1	1	24.9	-27.7
-8	1	1	28.1	-33.3
-9	1	1	4.6$^{\times}$	-0.3
-10	1	1	9.1	-11.0
11	2	1	15.1	17.3
10	2	1	29.9	-35.7
9	2	1	25.8	-32.4
8	2	1	13.4	11.8
7	2	1	3.7$^{\times}$	-2.9
6	2	1	22.3	21.5
5	2	1	11.0	-9.0
4	2	1	35.9	-36.7
3	2	1	23.6	-19.8
2	2	1	43.8	44.3
1	2	1	82.6	104.9
0	2	1	114.9*	-151.3
-1	2	1	58.4	-66.5
-2	2	1	5.2	4.2
-3	2	1	13.1	5.2
-4	2	1	23.6	22.2
-5	2	1	4.6$^{\times}$	-1.4
-6	2	1	22.8	19.4
-7	2	1	19.3	-16.3
-8	2	1	37.3	32.1
-9	2	1	34.8	33.2
-10	2	1	20.8	-24.7
11	3	1	7.6	8.1
10	3	1	2.8$^{\times}$	0.7
9	3	1	10.1	11.6
8	3	1	7.8	-7.3
7	3	1	12.1	-10.8
6	3	1	82.6	-85.7
5	3	1	7.1	-5.2
4	3	1	74.8	78.1
3	3	1	53.6	-54.4
2	3	1	34.4	31.9
1	3	1	23.4	20.5
0	3	1	25.1	24.5
-1	3	1	52.6	62.7
-2	3	1	14.2	12.5
-3	3	1	19.8	-17.8
-4	3	1	115.8	-114.8
-5	3	1	15.9	-14.5
-6	3	1	42.3	41.3
-7	3	1	30.9	-27.6
-8	3	1	14.0	11.6
-9	3	1	5.4$^{\times}$	6.1
-10	3	1	5.0$^{\times}$	7.4
-11	3	1	10.4	12.9
11	4	1	9.9	13.8
10	4	1	11.0	11.9
9	4	1	20.0	-22.4
8	4	1	10.6	11.5
7	4	1	42.9	41.7
6	4	1	16.6	-14.2
5	4	1	10.1	9.9
4	4	1	40.4	-39.6
3	4	1	75.5	-79.7
2	4	1	22.8	-19.8
1	4	1	33.5	34.5
0	4	1	49.4	50.4
-1	4	1	54.9	-60.5
-2	4	1	26.4	27.6
-3	4	1	77.4	81.6
-4	4	1	31.4	-29.2
-5	4	1	35.6	29.4
-6	4	1	35.2	-36.7
-7	4	1	49.4	-46.7
9	5	1	19.6	-17.9
8	5	1	25.1	25.5
7	5	1	24.5	22.9
6	5	1	20.2	-14.9
5	5	1	21.1	18.1
4	5	1	47.0	46.7
3	5	1	46.8	46.0
2	5	1	68.2	-67.4
1	5	1	44.9	-45.7
0	5	1	31.3	-28.8
-1	5	1	69.9	-80.5
-2	5	1	63.1	72.4
-3	5	1	8.4	3.7
-4	5	1	20.9	-17.9
-5	5	1	4.6$^{\times}$	2.1
-6	5	1	23.4	21.0
-7	5	1	39.7	33.1
-8	5	1	31.1	-29.0
10	6	1	7.4	6.0
9	6	1	23.9	-22.1
8	6	1	22.8	-22.7
7	6	1	10.6	-8.4
6	6	1	20.8	18.4
5	6	1	3.7$^{\times}$	1.5
4	6	1	43.3	38.8
3	6	1	28.3	26.1
2	6	1	40.3	-35.6
1	6	1	73.6	78.9
0	6	1	16.1	17.3
-1	6	1	43.6	-48.5
-2	6	1	47.9	-52.5
-3	6	1	37.6	-32.0
-4	6	1	13.3	9.9
-5	6	1	20.4	-16.3
-6	6	1	31.4	26.4
-7	6	1	11.6	-8.7
-8	6	1	14.2	-11.8
-9	6	1	26.4	22.3
-10	6	1	10.1	9.4
7	7	1	18.7	18.0
6	7	1	12.3	-9.0
5	7	1	61.1	-63.4
4	7	1	23.9	20.5
3	7	1	9.3	10.1
2	7	1	7.3	3.8
1	7	1	20.0	21.4
0	7	1	5.0$^{\times}$	-4.3
-1	7	1	32.6	32.5
-2	7	1	3.7	-1.7
-3	7	1	43.8	45.6
-4	7	1	16.6	-15.2
-5	7	1	62.4	-60.6
-6	7	1	10.1	6.5
9	8	1	6.5	6.6
8	8	1	14.2	-14.0
7	8	1	22.6	21.4
6	8	1	10.3	8.8
5	8	1	11.0	11.0
4	8	1	11.0	10.5
3	8	1	28.1	-25.7
2	8	1	32.9	-29.8
1	8	1	46.4	-51.4
0	8	1	43.6	47.3
-1	8	1	7.5	6.8
-2	8	1	20.4	-19.3
-3	8	1	42.9	41.1
-4	8	1	6.5$^{\times}$	2.7
-5	8	1	23.9	21.8
-6	8	1	15.1	10.8
-7	8	1	16.8	-12.5
-8	8	1	17.8	-13.7
-9	8	1	19.4	-16.3
-10	8	1	10.4	10.9
8	9	1	11.8	-10.2
7	9	1	13.3	13.0
6	9	1	12.7	12.2
5	9	1	3.5$^{\times}$	3.3
4	9	1	7.6	-6.5
3	9	1	38.8	39.1
2	9	1	7.6	4.4
1	9	1	23.6	-21.3
0	9	1	5.4$^{\times}$	-5.4
-1	9	1	38.8	-42.2
-2	9	1	9.5	-10.4
-3	9	1	17.0	19.2
-4	9	1	17.6	17.5
-5	9	1	4.8$^{\times}$	4.7
-6	9	1	5.2$^{\times}$	-7.5
-7	9	1	23.9	21.8
8	10	1	4.4	-6.8
7	10	1	20.0	-21.8
6	10	1	2.8$^{\times}$	-2.6
5	10	1	8.4	-6.4
4	10	1	3.3$^{\times}$	-3.5
3	10	1	32.0	29.7
2	10	1	9.3	-9.7
1	10	1	5.2$^{\times}$	-2.6
0	10	1	23.4	23.4
-1	10	1	9.7	8.6
-2	10	1	5.9$^{\times}$	-0.4
-3	10	1	27.7	-26.0
-4	10	1	4.6$^{\times}$	2.0
-5	10	1	4.4$^{\times}$	-5.8
-6	10	1	4.6$^{\times}$	0.5
-7	10	1	18.3	17.3
-8	10	1	13.1	-10.4
6	11	1	12.9	14.3
5	11	1	18.3	-19.3
4	11	1	18.3	-18.4
3	11	1	9.7	-10.2
2	11	1	3.7$^{\times}$	-4.8
1	11	1	8.9	8.2
0	11	1	7.3	-6.0
-1	11	1	19.1	17.9
-2	11	1	4.1$^{\times}$	-3.2
-3	11	1	8.4	6.3
-4	11	1	26.4	28.0
-5	11	1	15.1	-14.6
-6	11	1	4.1$^{\times}$	-6.1
-7	11	1	9.3	-7.8
5	12	1	4.6	4.4
4	12	1	3.7	4.2
3	12	1	2.8$^{\times}$	-1.2
2	12	1	3.0$^{\times}$	0.1
1	12	1	23.6	-27.5
0	12	1	11.2	-15.9
-1	12	1	13.4	13.9
-2	12	1	7.3	-8.6
-3	12	1	7.6	10.2
-4	12	1	3.7$^{\times}$	1.6
-5	12	1	3.5$^{\times}$	3.6
-6	12	1	7.4	6.9
2	13	1	12.3	16.0
1	13	1	5.0	-5.2
0	13	1	5.4	4.8
-1	13	1	9.9	-9.9
-2	13	1	11.0	-12.1
-3	13	1	7.4	-6.9
-4	13	1	2.8$^{\times}$	-1.8
-5	13	1	7.3	11.0
-10	0	2	15.3	19.8
-8	0	2	35.4	-49.9
-6	0	2	4.0$^{\times}$	-6.0
-4	0	2	21.7	21.8
-2	0	2	-	37.8
0	0	2	79.6*	121.5
2	0	2	94.7	-103.7
4	0	2	17.2	-16.9
6	0	2	4.2$^{\times}$	0.3
8	0	2	13.3	-10.9
10	0	2	27.9	33.6
-10	1	2	9.3	-8.6
-9	1	2	5.0$^{\times}$	0.7
-8	1	2	12.4	-13.6
-7	1	2	16.0	20.0
-6	1	2	5.2$^{\times}$	3.7
-5	1	2	31.0	-28.9
-4	1	2	80.2	83.4
-3	1	2	67.6	71.5
-2	1	2	-	6.2
-1	1	2	-	-48.1
0	1	2	42.0	-43.9
1	1	2	19.5	-18.4
2	1	2	45.3	-50.6
3	1	2	45.7	51.3
4	1	2	27.3	-24.6
5	1	2	37.2	-38.2
6	1	2	45.7	48.2
7	1	2	34.6	33.5
8	1	2	3.8$^{\times}$	2.7
9	1	2	17.0	-17.3
-9	2	2	13.7	-9.4
-8	2	2	11.0	-7.4
-7	2	2	24.8	24.1
-6	2	2	50.5	48.7
-5	2	2	24.8	-18.2
-4	2	2	9.3	9.6
-3	2	2	26.9	-24.2
-2	2	2	72.4	-79.3
-1	2	2	51.7	53.1
0	2	2	6.2	-4.6
1	2	2	31.7	-31.8
2	2	2	31.5	-25.9
3	2	2	42.8	39.9
4	2	2	68.6	69.3
5	2	2	28.3	-25.1
6	2	2	22.4	19.2
7	2	2	28.6	-29.3
8	2	2	35.2	-35.7
9	2	2	19.7	17.2
10	2	2	4.8	4.1
-10	3	2	15.3	15.0
-9	3	2	6.0$^{\times}$	-0.9
-8	3	2	22.8	18.6
-7	3	2	18.8	-14.7
-6	3	2	36.0	-35.3
-5	3	2	31.2	-28.0
-4	3	2	16.6	14.6
-3	3	2	36.8	37.5
-2	3	2	51.5	-61.6
-1	3	2	17.6	13.8
0	3	2	57.1	57.4
1	3	2	11.6	-7.4
2	3	2	66.8	66.7
3	3	2	11.2	-9.6
4	3	2	62.2	-56.3
5	3	2	30.0	-30.3
6	3	2	8.7	6.2
7	3	2	15.5	14.0
8	3	2	35.4	-34.6
9	3	2	5.8	5.1
10	3	2	3.4	9.4
-9	4	2	34.8	-32.9
-8	4	2	12.2	-10.6
-7	4	2	20.7	19.4
-6	4	2	31.5	-30.1
-5	4	2	17.6	12.9
-4	4	2	12.5	-5.8
-3	4	2	16.4	14.7
-2	4	2	34.1	34.9
-1	4	2	37.6	41.6
0	4	2	17.8	16.5
1	4	2	89.3	-97.1
2	4	2	21.1	-17.7
3	4	2	25.7	23.4
4	4	2	30.0	-31.8
5	4	2	4.2$^{\times}$	2.8
6	4	2	4.2$^{\times}$	-2.6
7	4	2	4.0$^{\times}$	-3.0
8	4	2	11.0	11.4
9	4	2	26.5	25.6
-8	5	2	11.4	-10.1
-7	5	2	11.0	7.1
-6	5	2	19.5	-16.4
-5	5	2	24.8	24.1
-4	5	2	52.3	61.9
-3	5	2	43.4	-45.3
-2	5	2	27.5	-26.6
-1	5	2	33.1	-32.1
0	5	2	14.3	-11.8
1	5	2	11.0	-9.3
2	5	2	4.2$^{\times}$	-0.3
3	5	2	25.9	17.8
4	5	2	31.7	-28.2
5	5	2	45.9	42.5
6	5	2	48.2	47.0
7	5	2	21.1	-18.3
8	5	2	10.2	-9.6
9	5	2	6.5	-7.0
-10	6	2	10.0	-8.4
-9	6	2	-	-3.2
-8	6	2	17.2	16.1
-7	6	2	14.7	12.6
-6	6	2	5.2$^{\times}$	-5.2
-5	6	2	31.5	-29.7
-4	6	2	4.2$^{\times}$	-1.5
-3	6	2	38.5	-41.3
-2	6	2	3.8$^{\times}$	2.1
-1	6	2	28.4	27.1
0	6	2	45.7*	-47.0
1	6	2	18.8	15.0
2	6	2	49.0	43.5
3	6	2	48.2	46.6
4	6	2	4.4$^{\times}$	2.5
5	6	2	17.8	-13.8
6	6	2	4.0$^{\times}$	-1.6
7	6	2	30.6	-27.5
8	6	2	2.9$^{\times}$	2.9
9	6	2	9.3	11.2
-7	7	2	28.1	-28.9
-6	7	2	5.0$^{\times}$	-3.1
-5	7	2	4.8$^{\times}$	8.6
-4	7	2	4.2$^{\times}$	-0.8
-3	7	2	10.2	-8.2
-2	7	2	18.0	-19.7
-1	7	2	56.6	60.3
0	7	2	8.1	6.3
1	7	2	11.8	12.7
2	7	2	22.0	20.7
3	7	2	48.6	-46.7
4	7	2	4.2$^{\times}$	-4.1
5	7	2	9.8	8.4
6	7	2	3.4$^{\times}$	1.7
7	7	2	19.5	-17.8
-9	8	2	10.8	-9.7
-8	8	2	13.5	12.1
-7	8	2	4.8$^{\times}$	-2.0
-6	8	2	12.2	-12.7
-5	8	2	22.8	23.2
-4	8	2	4.4$^{\times}$	1.6
-3	8	2	22.0	21.4
-2	8	2	21.3	24.3
-1	8	2	20.3	-18.5
0	8	2	25.7	-23.7
1	8	2	30.2	-27.9
2	8	2	29.8	28.2
3	8	2	14.3	-12.1
4	8	2	13.9	-13.1
5	8	2	20.9	18.2
6	8	2	3.1$^{\times}$	-2.7
7	8	2	14.1	13.0
8	8	2	9.1	12.1
-7	9	2	10.6	8.1
-6	9	2	10.0	10.1
-5	9	2	28.8	26.8
-4	9	2	12.6	-9.5
-3	9	2	27.7	-27.3
-2	9	2	4.4$^{\times}$	2.7
-1	9	2	14.7	-12.1
0	9	2	8.1	-7.3
1	9	2	4.2$^{\times}$	0.1
2	9	2	4.2$^{\times}$	1.1
3	9	2	11.0	7.5
4	9	2	13.5	13.4
5	9	2	33.1	31.5
6	9	2	13.9	-12.2
7	9	2	14.1	-15.8
-6	10	2	8.3	-5.6
-5	10	2	4.4$^{\times}$	-3.1
-4	10	2	4.4$^{\times}$	-3.2
-3	10	2	11.2	-12.1
-2	10	2	12.6	12.9
-1	10	2	9.8	-13.6
0	10	2	7.9	-6.3
1	10	2	31.9	35.2
2	10	2	7.3	7.6
3	10	2	3.4$^{\times}$	-0.8
4	10	2	11.0	-9.8
5	10	2	10.2	-8.3
6	10	2	5.0	-5.4
-7	11	2	5.8	-6.7
-6	11	2	11.6	14.1
-5	11	2	3.6$^{\times}$	-4.1
-4	11	2	3.8$^{\times}$	-1.8
-3	11	2	7.7	3.8
-2	11	2	10.6	10.6
-1	11	2	14.3	15.1
0	11	2	9.8	-12.3
1	11	2	3.2$^{\times}$	0.8
2	11	2	12.9	-12.6
3	11	2	18.6	-17.6
4	11	2	9.4	9.6
5	11	2	4.4	-6.3
-5	12	2	7.7	11.1
-4	12	2	2.9$^{\times}$	-2.1
-3	12	2	9.4	11.8
-2	12	2	9.4	-12.1
-1	12	2	10.0	-13.0
0	12	2	5.8	-6.7
1	12	2	2.7$^{\times}$	-0.1
2	12	2	2.5$^{\times}$	-1.7
3	12	2	8.3	-10.8
-1	13	2	6.2	-11.7
0	13	2	3.6	4.8

motion parameters and their associated e.s.d.s. were calculated from the results of the last refinement cycle by the Busing–Levy program ORXFE. The errors quoted include allowance for errors in cell dimensions. The best molecular plane was obtained by the method of Schomaker, Waser, Marsh & Bergman (1959), with bromine and carbon given relative weights of 50 and 1 respectively. The displacements (rounded off in accordance with experimental accuracy of coordinates) are given in the caption to Fig. 1.

Table 2. *Atomic parameters and estimated standard deviations from final least-squares cycle*

Temperature factor $= \exp\{-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+2hk\beta_{12}+2hl\beta_{13}+2kl\beta_{23})\}$ for bromine atoms
$= \exp\{-B\sin^2\theta/\lambda^2$ for carbon atoms
(carbon temperature factors from last cycle with isotropic temperature factors)

	Fractional coordinates				Temperature factors					
Atom	u	v	w	B	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Br(1)	0·0949	0·2796	0·0651		0·0119	0·0077	0·069	−0·0012	−0·0018	−0·0005
	$0\cdot0002_6$	$0\cdot0002_0$	0·0008		0·0003	0·0002	0·013	0·0002	0·0007	0·0005
Br(2)	0·3026	0·0651	0·4800		0·0085	0·0101	0·049	−0·0007	−0·0059	−0·0007
	$0\cdot0002_2$	$0\cdot0002_0$	0·0008		0·0003	0·0002	0·012	0·0002	0·0006	0·0005
C(1)	0·1240	0·0285	0·2017	2·35 Å²						
	0·0016	0·0013	0·0058	0·42						
C(2)	0·0397	0·1218	0·0277	2·42						
	0·0017	0·0014	0·0058	0·44						
C(3)	0·0802	−0·0881	0·1870	3·42						
	0·0020	0·0016	0·0069	0·56						

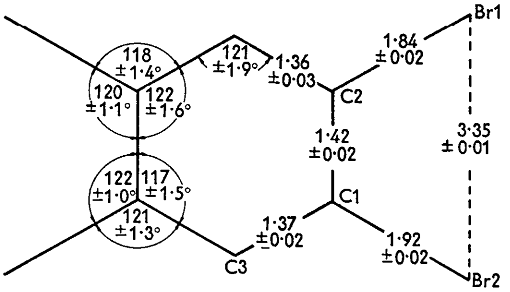


Fig. 1. Molecular dimensions with their estimated standard deviations. No corrections have been applied for thermal vibrations. The displacements of the atoms from the best molecular plane are:

Br(1)	0·001 Å	C(1)	0·01 Å
Br(2)	−0·001	C(2)	0·02
		C(3)	0·09

A positive displacement means that the atom in question is on the 0,0,$\bar{1}$ side of the plane.

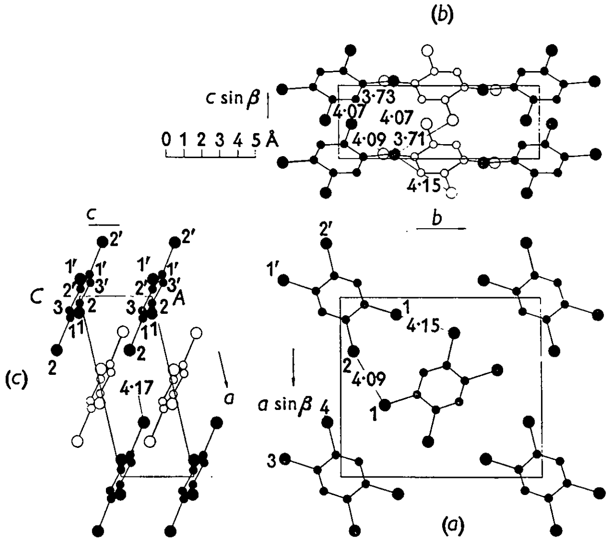
Molecular dimensions

The molecular dimensions are shown in Fig. 1. The equation of the molecular plane is

$$-0\cdot6119x'+0\cdot1092y+0\cdot7834z'=0$$

where x' and y are measured in Å along [100] and [010] respectively while z' is perpendicular to both [100] and [010]. Neither the asymmetry in the molecule nor the deviations from planarity are significant and these results are compatible with, but less accurate than, the values obtained for the β phase (Gafner & Herbstein, 1963).

It seems unlikely that much reliance can be placed on the thermal motion parameters derivable from the β_{ij} of Table 1 and these parameters will therefore not be reported.



γ-1,2 : 4,5-Tetrabromobenzene

Fig. 2. Molecular arrangement and shorter intermolecular distances (e.s.d.'s are Br · · · Br 0·01 Å, Br · · · C 0·025 Å, C · · · C 0·04 Å). Many symmetry-related distances have not been included. Projections of unit-cell contents down (*a*) [001], (*b*) [100] and (*c*) [010] are shown.

The shorter intermolecular distances (Å) within a stack are:

A	*C*	γ phase	β phase
Br(1)	Br(1)	4·07	4·009
Br(2)	Br(2)	4·07	4·009
Br(2)	Br(1)	4·25	4·076
Br(2)	C(1)	3·81	3·83
Br(2)	C(2)	3·88	3·88
C(1)	C(2)	3·80	3·71
C(1)	C(3')	3·64*	3·75
C(3)	C(2')	3·68*	3·76

* These distances are less than the interplanar distance because of the (not significant) displacement of C(3) from the molecular plane.

Molecular arrangements

The molecular arrangements in the two phases are very similar: that for the γ phase is shown in Fig. 2 while that for the β phase is given in Fig. 3 of Gafner & Herbstein (1963). For convenience corresponding intermolecular distances for both phases are given in the caption to Fig. 2 and in the body of this discussion (values for the β phase in brackets).

The molecules are arranged in stacks parallel to [001], each stack being surrounded by four others. The molecules in a stack are all parallel and make an angle of 38° 25′ (β: 36° 14′) with (001); the angle between the planes of molecules in two stacks related by the a-glide plane is 12° 32′ (β: 22° 22′). The interplanar distance within a stack is 3·69 Å (β: 3·363 Å). Part of this difference in interplanar spacing between the two phases may be due to inaccuracy in the present measurements of [001]. Adjacent molecules within a stack are staggered to avoid direct overlap of atoms; the normal projection of two molecules in the same stack separated by unit translation along [001] is shown in Fig. 3 for both phases. The arrangement in the γ phase differs from that in the β phase only by a relative shift along the Br(1)–Br(1′) direction of about 0·4 Å. There are some appreciable differences in the magnitudes of corresponding intermolecular distances in the two polymorphs. In the β phase the main intermolecular bonding appears to be between bromine atoms in different stacks, with approximately equal numbers of close contacts between molecules at the same level along [001] and those separated by unit translation along [001]. In the γ phase contacts between molecules at the same level along [001] appear to be less important.

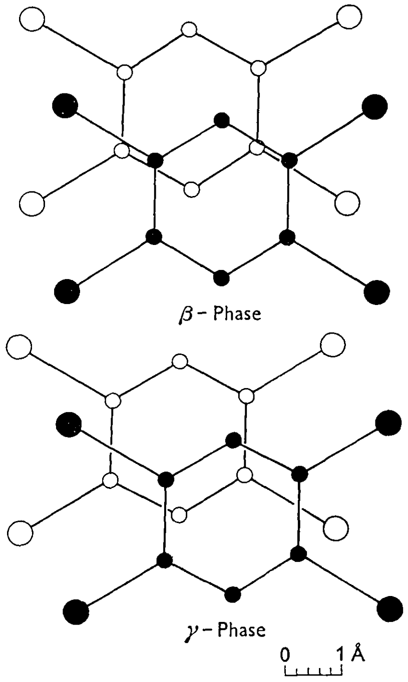


Fig. 3. Normal projection of two molecules in the same stack separated by unit translation along [001]: comparison of β and γ phases.

The differences in the cell dimensions of the β phase at 20 °C and the γ phase at 59 °C are:

$$\delta a = -3{\cdot}1\%,\quad \delta b = +4{\cdot}5\%,\quad \delta c = +1{\cdot}3\%,\quad \delta\beta = +1{\cdot}4\%.$$

However it has been shown by dilatometer measurements that the actual volume change at the transition temperature is less than 0·1% (Everett & Edwards, 1958). No detailed studies have been made of the mechanism of the phase transformation.

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