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The Crystal and Molecular Structures of Overcrowded Halogenated Compounds. Part II: β-1:2-4:5-Tetrabromobenzene

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The crystal structure of β-1:2-4:5-tetrabromobenzene (the polymorph stable at room temperature) has been determined by a three-dimensional least-squares analysis, using separate but isotropic temperature factors for individual C and Br atoms. The molecules are planar to within the accuracy of the measurements; the distance between adjacent bromine atoms is $3{\cdot}377 \pm 0{\cdot}004$ Å, an increase of $\sim 0{\cdot}08$ Å over that in the hypothetical regular molecule. An approximate calculation has been made, using published van der Waals functions, of the conformations expected for 1:2-4:5-tetrahalogenated benzenes. A general survey of available results for polychlorinated and polybrominated benzenes leads to the conclusion that these molecules are planar in the solid state, but the situation in the fluid states is still uncertain. The molecular arrangement and twinning in β-1:2-4:5-tetrabromobenzene is discussed.

1. Introduction

1:2-4:5-tetrabromobenzene is an example of a molecule which is overcrowded because of the presence of bulky substituents in the ortho positions of a benzene ring. Two polymorphic phases of this compound are found (Johnson, 1956; Gafner & Herbstein, 1960) and the present paper deals with the three-dimensional analysis of the crystal structure of the β phase which is stable at room temperature. The crystal structure of the γ-phase, stable above 46 °C., will be reported later.

Earlier work on the structures of polyhalogenated benzenes containing halogen atoms bonded to adjacent carbon atoms is reviewed later in this paper (Section **3**, 3). A preliminary report of the present results has been published (Gafner & Herbstein, 1958).

2. Experimental

(1) *Crystallographic data*

1:2-4:5-tetrabromobenzene was obtained from British Drug Houses (Laboratory Chemicals Group), Poole, England and recrystallized from ethanol–xylene mixtures. Crystallographic data were obtained from suitable Weissenberg and oscillation photographs, using Cu $K\alpha$ radiation ($\lambda\alpha_1 = 1{\cdot}54051$ Å, $\lambda\alpha_2 = 1{\cdot}54433$ Å).

$$a = 10{\cdot}323 \pm 0{\cdot}001,\ b = 10{\cdot}705 \pm 0{\cdot}001,$$
$$c = 4{\cdot}018 \pm 0{\cdot}004\ \text{Å},\ \beta = 102°\ 22' \pm 6',$$

space group $P2_1/a$.

$\varrho_{\text{meas.}} = 3{\cdot}027$ g.cm.$^{-3}$ (Handbook of Chemistry and Physics).

$\varrho_{\text{X-ray}} = 3{\cdot}014$ g.cm.$^{-3}$.

Linear absorption coefficient for Cu $K\alpha$ 231 cm.$^{-1}$, Mo $K\alpha$ 203 cm.$^{-1}$.

Many of the β-1:2-4:5-tetrabromobenzene crystals were found to be twinned and this is discussed in more detail below (Section **4**, 2).

(2) *Intensity measurements*

The intensities of 786 $hk0$, $hk1$, $hk2$ and $hk3$ reflexions (of which 92 had $I_o = 0$) were measured with Cu $K\alpha$ (Ni filter) radiation on an equi-inclination Weissenberg camera, using the standard multiple-film technique. The measured intensities, which covered a range of about 2000 to 1, were corrected for absorption on the justified assumption that the needle-shaped crystals were cylindrical (Buerger & Niizeki, 1958). The Lorentz, polarization, spot-shape (Phillips, 1954; 1957) and absorption corrections were applied simultaneously to each reflexion using a plot of the reciprocal lattice. The individual layers were put on an approximately absolute scale by Wilson's (1942) method. Further adjustments of about 10% in $F_{\text{abs.}}$ were made later by comparing observed and calculated structure factors.

(3) *Determination of approximate atomic positions*

The present structure is particularly well-suited to the employment of Patterson methods for determining approximate bromine positions. The $hk0$ Patterson projection and generalized $hk2$ Patterson projection are shown in Figs. 1 and 2 respectively. The F^2 values were multiplied by the modification function $M(s) = (\hat{f})^{-2} \exp(-\sin^2\theta/\lambda^2)$ in both instances (Lipson & Cochran, 1953). The first clue to the structure was given by the identification of peaks A and B (Fig. 1) as single-weight intramolecular Br $\cdots$ Br vectors. Identification of the other peaks followed at once and led to the mean u and v bromine co-ordinates given in Table 1. The w co-ordinates of the atoms could be

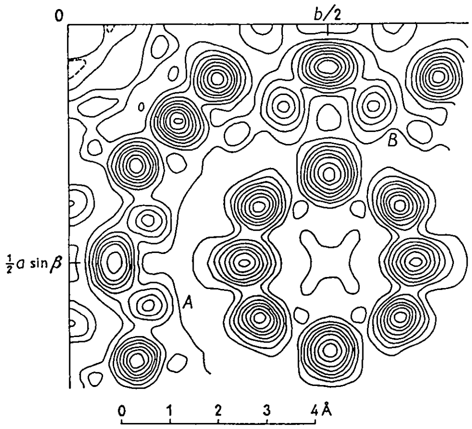

Fig. 1. Modified *hk*0 Patterson projection. Contours are at equal but arbitrary intervals, with zero contour dashed. Contours in the origin peak have been omitted.

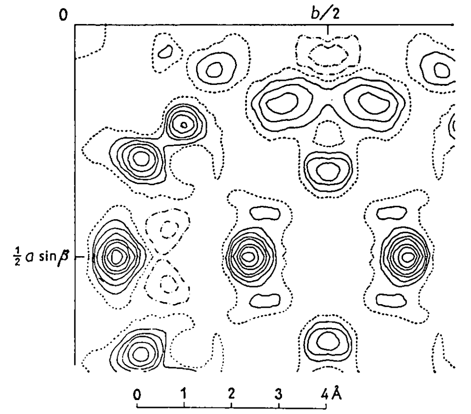

Fig. 2. Modified generalized *hk*2 Patterson projection. Contours are at equal but arbitrary intervals, with zero contour dashed and negative contours dot-dashed. Contours in the origin peak have been omitted.

obtained in the usual way by comparing the heights of corresponding peaks in the *hk*0 and *hk*2 projections but this method requires that both sets of intensities are accurately on the same scale. This difficulty is avoided by using the Harker peaks with $\Delta w=0$ as internal standards in the analysis of the *hk*2 projection. The peak heights in the *hk*2 generalized Patterson projection yield a number of possible w_i values because of the periodicity of the cosine function. The correct values were chosen by comparing the results of structure-factor computations with the observed F values (it is essential that reflexions with l odd be included in these comparisons). In retrospect it is clear that it would have been better to have computed the *hkl* generalized Patterson function to reduce the effect of these ambiguities.

Preliminary carbon co-ordinates were then calculated on the assumption of a regular planar model with standard bond lengths and angles.

(4) *Refinement of atomic co-ordinates*

Because of the incompleteness of the intensity data the refinement of the atomic co-ordinates was carried through by least squares rather than Fourier methods. Accordingly the data were sent to the Service Bureau Corporation, New York, for refinement on the IBM 704 computer, using the programme NY XR2 developed by Dr D. Sayre. In this programme co-ordinates and an isotropic temperature factor for each atom, as well as an overall scale factor, are refined together. The function minimized is

$$R' = \sum_{hkl} w_{hkl}[k|F_m| - |F_c|]^2,$$

where F_m is the measured structure factor on a relative scale, w_{hkl} is the weighting factor for the *hkl* reflexion, and k is the overall scale factor.

The weighting factors were derived from a comparison of two independent sets of measurements of the *hk*0 intensities (cf. Ibers, 1956). The variation of weight with $|F_m|$ is similar to that given by other authors (Abrahams, 1955; Ibers & Cromer, 1958). For reflexions below the observation limit $F_{\text{min.}}$ we have used the scheme proposed by Hamilton (1955):

$$w=2{\cdot}45\,(F_{\text{min.}})^{-1},\quad F_{\text{unobs.}} \sim \tfrac{1}{2}F_{\text{min.}}\,.$$

The atomic scattering factor used for bromine is that calculated by the Thomas–Fermi–Dirac method (Thomas & Umeda, 1957) and thus includes the effect of exchange. The appropriate correction for anomalous dispersion (Dauben & Templeton, 1955) was applied. For carbon the *f*-curve for the valence state, with inclusion of exchange (Berghuis *et al.*, 1955) was used. The hydrogen-atom contributions were not included.

The refinement proceeded steadily and was stopped after seven stages, when the changes in the parameters were about as large as their standard deviations.

Comparison of the final observed and calculated

Table 1. *Initial and final fractional atomic coordinates*

	Coordinates from Patterson projections and idealised model			Final coordinates from least-squares refinement			
Atom	*u*	*v*	*w*	*u*	*v*	*w*	*B*
Br 1	0·093	0·293	−0·026	0·0891	0·2930	−0·0272	3·21 Å^2
Br 2	0·296	0·079	0·419	0·2951	0·0784	0·4246	2·99
C 1	0·124	0·039	0·173	0·1229	0·0343	0·1680	2·9
C 2	0·040	0·121	−0·008	0·0376	0·1243	−0·0113	2·5
C 3	0·083	−0·087	0·182	0·0900	−0·0897	0·1950	3·1

structure factors (Table 2) showed that sixteen of the stronger reflexions suffered from extinction; these all had small weighting factors and thus would not affect the final parameters materially. In calculating the final R factor they were not included while unobserved reflections were given values $\frac{1}{2}F_{\text{min.}}$.

The final R factor is 15·3% while the value of

$$R_2 = \{\sum_{hkl} w(F_o-F_c)^2/\sum_{hkl} wF_o^2\}^{\frac{1}{2}}$$

is 22·1%. The latter value is the more significant as it was the numerator $(=R')$ which was actually minimized. A comparable value reported recently for R_2 is 25% for the least-squares refinement of gold(III)-chloride (Clark, Templeton & MacGillavry, 1958).

(5) *Difference synthesis down* [001]

The refinement reported here was made with the assumption of separate, but isotropic, temperature factors for each atom as no facilities for introducing anisotropic temperature factors were available to us. It was felt, however, that a qualitative indication of the type of thermal motion was desirable and that

Table 2. *Observed and calculated structure factors*

hkl	$\lvert F_o\rvert$	F_c
000	-	356
020	12.6	-10.1
040	3.3	-6.2
060	58.1	-74.4
080	49.5	-61.5
0,10,0	30.9	39.9
0,12,0	10.7	-2.7
200	22.4	-23.0
400	28.7	-31.5
600	49.5	-64.2
800	34.0	-39.2
10,0,0	39.3	54.6
12,0,0	6.8	-5.2
110	14.2	-14.9
120	54.4	-64.4
130	52.5	59.8
140	101.2	-130.6x
150	56.7	-62.3
160	20.5	20.3
170	55.1	65.7
180	1.3	7.2+
190	17.2	-16.3
1,10,0	32.1	37.1
1,11,0	1.3	-2.8+
1,12,0	6.8	9.2
210	59.5	-74.0x
220	72.4	-90.0x
230	94.6	116.4x
240	33.7	34.2
250	5.0	8.9
260	48.3	55.6
270	29.5	-34.3
280	17.8	22.0
290	1.3	-3.0+
2,10,0	9.4	7.9
2,11,0	35.6	-38.5
2,12,0	22.5	-29.0
2,13,0	16.0	17.1
310	59.0	69.7
320	84.8	105.3x
330	12.1	-14.2
340	21.1	-19.5
350	39.4	-42.0
360	63.3	68.7
370	38.2	-41.8
380	57.3	-67.9
390	1.4	-2.2+
3,10,0	6.6	-14.4
3,11,0	8.3	12.1
3,12,0	1.0	-3.0+
3,13,0	8.7	12.4
410	86.3	-111.4x
420	52.0	53.6
430	28.5	-29.0
440	41.2	-41.4
450	40.4	-43.3
460	23.0	-24.1
470	1.3	1.9+
480	7.6	5.8
490	38.9	47.6
4,10,0	10.9	-13.1
4,11,0	8.0	-2.9
4,12,0	17.3	19.0
4,13,0	9.4	11.3
510	56.2	-62.2
520	1.0	-0.5+
530	56.3	-61.2
540	20.7	-23.1
550	84.8	100.8
560	26.3	24.0
570	1.3	7.6+
580	7.7	-4.6
590	31.0	29.1
5,10,0	3.5	5.9
5.11.0	18.9	-19.7
610	41.0	41.1
620	47.7	55.1
630	45.9	49.6
640	24.8	-26.0
650	40.8	42.7
660	5.5	-3.8
670	5.5	-1.6
680	14.3	16.2
690	22.7	-31.5
6,10,0	25.7	-21.6
6,11,0	7.9	-11.7
6,12,0	11.3	15.3
710	49.0	56.9
720	40.6	-46.1
730	17.9	-18.3
740	9.2	11.3
750	1.4	2.5+
760	23.3	-21.6
770	41.7	-51.2
780	26.6	29.8
790	1.1	3.3+
7,10,0	1.0	2.3+
7,11,0	4.8	6.8
810	17.7	20.0
820	8.5	-3.7
830	57.0	-68.9
840	15.1	10.5
850	7.8	-8.6
860	19.8	22.2
870	16.6	20.1
880	16.9	13.3
890	1.0	1.7+
8,10,0	6.2	-7.6
910	16.5	-19.8
920	3.8	0.9
930	7.3	9.8
940	38.6	48.5
950	8.3	5.6
960	18.9	-19.0
970	18.6	18.6
980	2.9	3.6
990	5.5	-2.0
10,1,0	15.8	19.4
10,2,0	1.3	-1.8+
10,3,0	7.2	-8.3
10,4,0	1.2	0.3+
10,5,0	1.1	6.8+
10,6,0	21.9	-22.4
10,7,0	0.9	1.9+
10,8,0	15.4	-21.0
11,1,0	7.3	-6.9
11,2,0	24.2	-24.5
11,3,0	14.1	16.2
11,4,0	17.1	-19.8
11,5,0	15.4	-19.9
11,6,0	5.5	-5.9
11,7,0	7.6	11.5
12,1,0	3.5	-5.2
12,2,0	20.7	-25.7
12,3,0	8.9	10.2
12,4,0	10.5	13.5
201	81.1	148.6x
401	75.5	-107.1x
601	29.1	-30.9
801	2.4	-1.5+
10,0,1	11.6	-4.4
12,0,1	20.6	27.9
$\bar{2}01$	97.4	131.3x
$\bar{4}01$	53.3	-56.6
$\bar{6}01$	89.5	-112.8x
$\bar{8}01$	35.9	37.6
$\overline{10}$,0,1	9.3	-5.9
011	-	0.4
021	90.9	-131.0x
031	50.7	-49.0
041	56.8	59.5
051	24.2	23.9
061	53.9	60.1
071	2.5	1.3+
081	2.5	8.7+
091	11.0	6.2
0,10,1	28.9	22.2
0,11,1	14.7	12.2
0,12,1	37.3	-42.1
111	39.2	-39.5
121	72.1	106.9x
131	49.2	49.2
141	49.1	48.2
151	60.9	-60.6
161	31.0	28.7
171	57.0	62.7
181	51.1	-56.9
191	21.9	-17.6
1,10,1	35.4	-31.7
211	59.5	-81.0x
221	9.9	-8.5
231	41.4	41.2
241	23.4	-19.4
251	18.8	-15.8
261	53.4	-55.3
271	22.4	-15.8
281	38.3	-39.5
291	25.7	20.3
2,10,1	30.2	22.4
2,11,1	23.9	-19.6
2,12,1	1.8	6.2+
2,13,1	12.7	12.9
311	42.9	-43.7
321	33.2	-25.9
331	15.8	-11.1
341	91.2	-121.1x
351	15.3	13.8
361	51.8	50.0
371	28.1	26.2
381	11.0	-5.3
391	9.4	4.7
3,10,1	43.1	36.8
3,11,1	4.5	-7.8
3,12,1	8.6	8.9
411	45.9	-47.4
421	13.9	-10.3
431	66.4	81.3
441	6.6	2.7
451	24.1	18.9
461	45.4	42.6
471	15.4	-12.7
481	33.0	34.6
491	9.2	3.1
4,10,1	24.2	-16.7
4,11,1	30.8	-28.6
511	56.6	63.3
521	46.9	39.0
531	34.7	-33.8
541	10.0	7.6
551	15.7	11.6
561	35.0	35.9
571	59.2	-59.0
581	25.8	-21.7
591	13.3	9.4
5,10,1	11.8	-8.7
611	31.4	-29.7
621	51.4	60.5
631	56.9	-58.2
641	30.1	-26.6
651	25.5	-21.5
661	17.3	-13.9
671	18.0	17.5
681	14.5	9.1
691	30.1	24.1
6,10,1	21.6	-17.9
6,11,1	13.0	13.0
711	32.3	-25.5
721	26.4	-24.8
731	28.2	-26.1
741	17.3	14.2
751	62.3	58.1
761	17.8	-14.8
771	11.4	5.6
781	20.4	14.5
791	17.7	16.6
7,10,1	7.7	-4.6
811	42.5	47.4
821	25.2	20.6
831	15.5	7.0
841	2.8	-8.6+
851	33.3	24.8
861	15.0	-8.6
871	2.2	0.3+
881	2.0	-0.2+
891	32.7	-32.1
911	26.1	24.9
921	33.0	-32.4
931	2.5	6.1+
941	2.4	8.5+
951	29.2	-23.1
961	27.7	-23.7
971	20.9	-16.9
981	18.3	18.4
10,1,1	4.8	8.0
10,2,1	27.7	-24.6
10,3,1	34.4	-30.2
10,4,1	15.3	12.4
10,5,1	8.6	-5.6
10,6,1	12.1	12.1
10,7,1	9.4	6.8
11,1,1	20.5	-16.7
11,2,1	16.8	12.7
11,3,1	12.0	11.4
11,4,1	23.5	20.8
11,5,1	7.2	-8.5
$\bar{1}11$	-	85.6
$\bar{1}21$	69.7	-88.5
$\bar{1}31$	55.0	58.0
$\bar{1}41$	7.2	-4.5
$\bar{1}51$	84.5	-105.2
$\bar{1}61$	53.9	-57.9
$\bar{1}71$	9.9	3.0
$\bar{1}81$	49.0	47.1
$\bar{1}91$	24.6	-23.9
$\bar{1}$,10,1	10.8	14.0
$\bar{1}$,11,1	17.1	13.7
$\bar{1}$,12,1	2.0	4.8+
$\bar{1}$,13,1	12.1	14.3
$\bar{2}11$	102.3	151.4x
$\bar{2}21$	26.6	22.6
$\bar{2}31$	31.1	28.6
$\bar{2}41$	22.5	-15.8
$\bar{2}51$	58.8	56.3
$\bar{2}61$	35.7	-36.9
$\bar{2}71$	2.5	2.0+
$\bar{2}81$	24.5	-21.2
$\bar{2}91$	47.5	-57.9
$\bar{2}$,10,1	15.0	12.4
$\bar{2}$,11,1	17.4	8.4
$\bar{2}$,12,1	1.9	2.8+
$\bar{2}$,13,1	14.4	-13.0
$\bar{3}11$	53.4	-55.8
$\bar{3}21$	23.1	-17.9
$\bar{3}31$	32.4	-29.4
$\bar{3}41$	78.3	87.8
$\bar{3}51$	59.7	62.1
$\bar{3}61$	55.7	-53.2
$\bar{3}71$	31.7	35.2
$\bar{3}81$	35.2	33.2
$\bar{3}$,9,1	25.7	19.5
$\bar{3}$,10,1	19.1	-13.9
$\bar{3}$,11,1	18.2	-17.3
$\bar{3}$,12,1	1.9	-3.2+
$\bar{3}$,13,1	11.3	-18.7
$\bar{4}11$	20.8	18.7
$\bar{4}21$	56.6	53.4
$\bar{4}31$	92.1	-112.3
$\bar{4}41$	42.6	-35.6
$\bar{4}51$	32.7	-32.4
$\bar{4}61$	9.9	-7.9
$\bar{4}71$	32.2	29.5
$\bar{4}81$	18.9	18.1
$\bar{4}91$	21.8	25.1
$\bar{4}$,10,1	21.6	-16.7
$\bar{4}$,11,1	39.1	37.2
$\bar{4}$,12,1	17.2	14.9
$\bar{5}11$	70.3	79.1
$\bar{5}21$	16.5	15.3
$\bar{5}31$	53.2	-51.5
$\bar{5}41$	29.1	24.7
$\bar{5}51$	11.0	7.7
$\bar{5}61$	11.5	-8.1
$\bar{5}71$	69.6	-80.4
$\bar{5}81$	2.7	1.4+
$\bar{5}91$	21.4	13.4
$\bar{5}$,10,1	2.3	-4.9+
$\bar{5}$,11,1	12.4	11.5
$\bar{6}11$	8.9	3.7
$\bar{6}21$	23.8	22.7
$\bar{6}31$	58.9	64.4
$\bar{6}41$	14.8	-13.3
$\bar{6}51$	11.7	15.1
$\bar{6}61$	25.3	25.0
$\bar{6}71$	19.0	-17.2
$\bar{6}81$	38.4	32.0
$\bar{6}91$	15.4	-11.9
$\bar{6}$,10,1	25.2	-22.2
$\bar{6}$,11,1	14.6	-18.6
$\bar{6}$,12,1	6.8	5.6
$\bar{7}11$	31.2	-31.2
$\bar{7}21$	15.7	-11.7
$\bar{7}31$	26.8	-25.1
$\bar{7}41$	70.8	-74.5
$\bar{7}51$	50.5	50.4
$\bar{7}61$	22.0	17.9
$\bar{7}71$	2.6	4.5+
$\bar{7}81$	9.0	-4.2
$\bar{7}91$	11.5	12.9
$\bar{7}$,10,1	27.0	25.0
$\bar{7}$,11,1	5.3	-10.1
$\bar{8}11$	46.0	-51.6
$\bar{8}21$	25.7	26.3
$\bar{8}31$	13.2	13.7
$\bar{8}41$	11.0	-10.7
$\bar{8}51$	23.9	-22.8
$\bar{8}61$	32.4	-27.5
$\bar{8}71$	14.7	-10.9
$\bar{8}81$	14.2	-16.9
$\bar{8}91$	26.1	23.8
$\bar{9}11$	2.7	-1.5+
$\bar{9}21$	47.8	54.8
$\bar{9}31$	16.4	17.6
$\bar{9}41$	2.6	7.1+
$\bar{9}51$	14.0	-12.0
$\bar{9}61$	28.5	25.1
$\bar{9}71$	14.0	8.2
$\bar{9}81$	32.2	-33.6
$\bar{9}91$	10.1	-8.4
$\overline{10}$,1,1	16.1	-13.9
$\overline{10}$,2,1	37.8	-38.2
$\overline{10}$,3,1	9.0	10.0
$\overline{10}$,4,1	30.3	27.0
$\overline{10}$,5,1	2.3	-5.0+
$\overline{10}$,6,1	25.5	25.6
$\overline{10}$,7,1	6.8	-3.8
$\overline{11}$,1,1	2.4	3.3+
$\overline{11}$,2,1	16.3	-15.7
$\overline{11}$,3,1	19.4	20.5
$\overline{11}$,4,1	14.9	-15.1
$\overline{11}$,5,1	21.4	-25.6
$\overline{12}$,1,1	17.8	19.5
$\overline{12}$,2,1	2.0	-5.1+
$\overline{12}$,3,1	10.8	8.9
$\overline{12}$,4,1	1.6	2.1+
$\overline{12}$,5,1	10.6	10.9
002	70.7	117.7x
202	27.5	-22.6
402	49.7	44.8
602	52.9	-61.8
802	6.6	-7.2
10,0,2	10.3	11.7
$\bar{2}02$	-	23.2
$\bar{4}02$	75.8	-78.0
$\bar{6}02$	4.3	1.6
$\bar{8}02$	41.4	-45.6
$\overline{10}$,0,2	38.4	48.4
012	52.4	57.5
022	44.9	-42.5
032	46.4	43.0
042	7.9	7.1
052	35.0	29.7
062	26.6	-24.0
072	18.9	-13.0
082	32.3	-29.9
092	33.0	-37.6
0,10,2	24.8	24.5
0,11,2	5.4	-8.2
0,12,2	11.5	-8.5
112	16.0	12.2
122	39.2	-39.9
132	38.0	40.3
142	60.3	-57.3
152	75.6	-80.4
162	3.4	2.2
172	23.7	19.2
182	12.3	13.1
192	19.1	-21.6
1,10,2	18.4	21.5
1,11,2	11.2	9.7
1,12,2	6.3	5.3

– in F_o column: intensity not measured. × extinction error. + reflection not observed; $F_o = \frac{1}{2}F_{\text{min.}}$.

Table 2 (*cont.*)

$hk\ell$	$\|F_o\|$	F_c
212	59.5	-61.0
222	71.2	-83.1
232	3.0	4.0
242	36.5	33.8
252	15.4	-17.1
262	47.7	47.3
272	3.5	0.1
282	14.9	14.3
292	32.1	27.5
2,10,2	15.1	9.7
2,11,2	11.2	-7.3
2,12,2	15.0	-27.7
312	13.5	-10.0
322	64.7	74.2
332	6.2	4.0
342	11.3	4.9
352	2.3	-8.1+
362	52.1	55.1
372	18.1	15.1
382	35.6	-42.3
392	2.2	-1.4+
3,10,2	11.1	-12.1
3,11,2	4.2	-2.5
412	51.8	-59.4
422	44.4	46.1
432	20.6	17.7
442	30.3	-27.2
452	13.1	-9.1
462	37.1	-37.4
472	2.4	-0.4+
482	13.2	-13.0
492	23.4	24.5
4,10,2	1.7	-1.8+
4,11,2	11.6	-12.5
512	2.3	-0.9+
522	33.0	-27.6
532	26.4	-24.7
542	53.5	-58.0
552	36.3	39.1
562	22.0	19.8
572	6.6	-7.8
582	8.6	6.0
592	19.4	13.9
5,10,2	20.4	20.8
612	5.0	4.4
622	19.5	21.5
632	27.1	23.7
642	2.4	-6.8+
652	18.2	13.9
662	24.4	17.9
672	6.2	-4.7
682	25.7	23.4
692	14.2	-12.8
6,10,2	13.1	-16.0
712	32.1	38.9
722	8.5	2.6
732	16.1	-17.3
742	21.5	23.0
752	2.2	2.2+
762	9.6	-7.1
772	44.4	-37.8
782	5.5	-2.9
812	2.3	7.0+
822	13.7	-16.2
832	35.7	-42.7
842	13.4	-9.9
852	13.5	-9.8
862	13.6	-7.6
872	10.1	9.2
912	26.8	-23.4
922	11.7	-11.4
932	3.7	-3.3
942	19.0	18.7
952	17.7	14.5
962	9.8	-15.1
10,1,2	22.8	23.3
10,2,2	12.4	-6.4
$\bar{1}$12	-	-72.8
$\bar{1}$22	4.1	-1.5
$\bar{1}$32	25.3	21.9
$\bar{1}$42	65.9	64.9
$\bar{1}$52	7.4	6.6
$\bar{1}$62	45.7	-45.0
$\bar{1}$72	62.2	71.0
$\bar{1}$82	13.4	7.6
$\bar{1}$92	2.4	-2.3+
$\bar{1}$,10,2	21.5	-20.3
$\bar{1}$,11,2	13.3	-14.6
$\bar{2}$12	51.5	45.1
$\bar{2}$22	6.9	-1.3
$\bar{2}$32	108.7	-109.7
$\bar{2}$42	7.8	1.4
$\bar{2}$52	30.8	-28.0
$\bar{2}$62	4.7	2.9
$\bar{2}$72	21.5	19.8
$\bar{2}$82	2.3	1.9+
$\bar{2}$92	2.3	4.9+
$\bar{2}$,10,2	4.5	1.5
$\bar{2}$.11.2	32.9	38.0
$\bar{3}$12	100.3	91.9
$\bar{3}$22	4.8	-7.0
$\bar{3}$32	14.3	-13.4
$\bar{3}$42	73.5	66.5
$\bar{3}$52	27.4	-23.9
$\bar{3}$62	50.7	-45.4
$\bar{3}$72	64.2	-57.8
$\bar{3}$82	16.6	19.0
$\bar{3}$92	2.6	1.3+
$\bar{3}$,10,2	12.5	-13.7
$\bar{3}$,11,2	5.2	11.4
$\bar{4}$12	75.9	72.0
$\bar{4}$22	44.6	37.1
$\bar{4}$32	50.1	42.1
$\bar{4}$42	19.2	-16.3
$\bar{4}$52	36.8	35.9
$\bar{4}$62	20.0	16.8
$\bar{4}$72	2.4	-4.1+
$\bar{4}$82	24.9	28.8
$\bar{4}$92	26.2	-32.9
$\bar{4}$,10,2	21.2	-19.7
$\bar{4}$,11,2	5.0	-0.9
$\bar{4}$,12,2	5.8	5.2
$\bar{5}$12	16.4	-17.6
$\bar{5}$22	34.3	-29.6
$\bar{5}$32	52.1	-47.8
$\bar{5}$42	30.9	-32.9
$\bar{5}$52	68.4	67.3
$\bar{5}$62	2.4	-5.8+
$\bar{5}$72	13.3	-10.9
$\bar{5}$82	18.2	21.3
$\bar{5}$92	22.7	24.2
$\bar{5}$,10,2	23.0	21.7
$\bar{5}$,11,2	7.7	-10.2
$\bar{6}$12	41.0	-38.8
$\bar{6}$22	59.6	63.1
$\bar{6}$32	2.3	-4.6+
$\bar{6}$42	40.2	-39.7
$\bar{6}$52	22.7	-20.3
$\bar{6}$62	40.4	-38.8
$\bar{6}$72	2.4	0.7+
$\bar{6}$82	2.2	-4.9+
$\bar{6}$92	23.6	26.8
$\bar{6}$,10,2	10.6	-9.3
$\bar{7}$12	8.2	9.1
$\bar{7}$22	63.4	61.5
$\bar{7}$32	18.3	-15.9
$\bar{7}$42	2.4	2.0+
$\bar{7}$52	10.0	8.3
$\bar{7}$62	30.5	32.7
$\bar{7}$72	16.7	-19.0
$\bar{7}$82	33.9	-35.5
$\bar{7}$92	1.9	5.2+
$\bar{7}$,10,2	4.4	-8.5
$\bar{8}$12	37.3	-40.8
$\bar{8}$22	28.9	-29.8
$\bar{8}$32	16.8	20.5
$\bar{8}$42	20.0	17.8
$\bar{8}$52	13.0	-14.2
$\bar{8}$62	23.3	31.1
$\bar{8}$72	11.8	-9.9
$\bar{8}$82	16.6	14.3
$\bar{8}$92	17.2	17.2
$\bar{9}$12	2.4	1.4+
$\bar{9}$22	13.1	-14.0
$\bar{9}$32	14.7	17.9
$\bar{9}$42	44.5	-51.2
$\bar{9}$52	16.8	-20.2
$\bar{9}$62	7.5	10.2
$\bar{9}$72	8.8	5.2
$\bar{9}$82	1.6	0.3+
$\bar{9}$92	8.8	-9.8
$\overline{10}$,1,2	2.4	0.4+
$\overline{10}$,2,2	8.1	-8.5
$\overline{10}$,3,2	18.8	23.3
$\overline{10}$,4,2	9.8	8.2
$\overline{10}$.5.2	7.1	5.0
$\overline{10}$,6,2	11.1	-13.7
$\overline{10}$,7,2	10.1	-7.8
$\overline{10}$,8,2	13.1	-19.5
$\overline{11}$,1,2	22.6	-24.7
$\overline{11}$,2,2	10.8	24.5
$\overline{11}$,3,2	17.9	17.4
$\overline{11}$,4,2	14.1	17.2
$\overline{11}$,5,2	1.6	-1.2+
$\overline{11}$,6,2	1.2	-2.5+
$\overline{11}$,7,2	12.2	25.9
$\overline{12}$,1,2	1.7	5.3+
$\overline{12}$,2,2	11.1	-14.1
$\overline{12}$,3,2	14.3	-23.0
$\overline{12}$,4,2	8.1	11.1
003	-	31.1
203	-	69.8
403	36.0	-30.2
603	16.3	5.0
803	31.8	-27.6
$\bar{2}$03	-	-24.6
$\bar{4}$03	14.2	5.0
$\bar{6}$03	66.5	-68.0
$\bar{8}$03	32.2	33.8
013	3.9	-1.0
023	54.2	-45.6
033	68.5	-62.1
043	13.6	14.4
053	23.5	-21.6
063	3.9	8.7
073	15.6	14.4
083	5.1	-5.6
093	18.4	15.5
0,10,3	16.5	13.5
0,11,3	11.1	19.8
113	60.9	-52.2
123	18.9	14.9
133	22.5	21.3
143	17.2	13.5
153	3.4	-10.9+
163	14.9	7.1
173	60.9	55.4
183	3.0	-4.7+
193	4.5	-5.7
213	6.7	-9.9
223	11.8	-13.4
233	55.1	43.8
243	3.4	0.02+
253	20.3	15.0
263	21.3	-19.3
273	13.3	-5.7
283	21.6	-18.8
293	2.3	-3.2+
2,10,3	12.4	14.7
313	29.6	22.6
323	21.9	-13.2
333	13.3	11.2
343	51.2	-54.0
353	29.6	-28.0
363	21.0	24.5
373	2.9	-3.5+
383	2.6	1.1+
393	2.1	-6.0+
3,10,3	11.4	20.0
413	39.8	-39.9
423	13.4	-9.4
433	3.3	9.3+
443	11.3	7.0
453	11.0	-9.6
463	24.5	22.4
473	2.7	-2.7+
483	22.3	16.1
493	13.4	16.4
513	13.1	11.4
523	36.0	33.6
533	12.6	-13.0
543	15.1	7.0
553	17.4	12.6
563	20.5	20.7
573	13.5	-12.0
583	24.0	-24.5
613	13.6	-12.2
623	33.8	35.2
633	2.9	-3.9+
643	25.9	-20.7
653	7.0	-4.8
663	24.7	-21.0
713	9.8	-6.0
723	27.6	-19.9
733	18.0	-16.3
743	15.9	-11.0
753	21.0	22.6
813	17.3	18.6
823	2.0	1.1+
833	10.5	5.0
$\bar{1}$13	38.4	34.2
$\bar{1}$23	13.9	-15.1
$\bar{1}$33	15.3	14.8
$\bar{1}$43	38.9	36.2
$\bar{1}$53	48.7	-49.5
$\bar{1}$63	39.9	-33.6
$\bar{1}$73	16.3	-12.0
$\bar{1}$83	14.0	14.2
$\bar{1}$93	9.4	-11.7
$\bar{1}$,10,3	12.5	-9.7
$\bar{1}$,11,3	6.6	9.9
$\bar{2}$13	82.3	74.1
$\bar{2}$23	17.8	-10.6
$\bar{2}$33	22.7	14.0
$\bar{2}$43	6.8	4.3
$\bar{2}$53	31.6	26.7
$\bar{2}$63	24.9	17.1
$\bar{2}$73	3.3	-5.5+
$\bar{2}$83	13.5	11.6
$\bar{2}$93	40.2	-40.1
$\bar{2}$,10,3	2.2	-4.0+
$\bar{2}$,11,3	4.1	3.2
$\bar{3}$13	29.3	-22.4
$\bar{3}$23	49.2	-39.5
$\bar{3}$33	28.7	-21.7
$\bar{3}$43	12.6	4.9
$\bar{3}$53	45.0	46.0
$\bar{3}$63	38.1	-38.2
$\bar{3}$73	9.3	8.8
$\bar{3}$83	21.3	25.3
$\bar{3}$93	18.2	13.4
$\bar{3}$,10,3	2.9	5.7+
$\bar{3}$,11,3	8.5	-11.9
$\bar{4}$13	15.9	10.5
$\bar{4}$23	71.7	62.6
$\bar{4}$33	31.0	-28.5
$\bar{4}$43	27.0	-30.4
$\bar{4}$53	19.1	-11.8
$\bar{4}$63	25.8	-29.2
$\bar{4}$73	4.1	4.0+
$\bar{4}$83	3.9	1.9+
$\bar{4}$93	3.5	5.4+
$\bar{4}$,10,3	11.4	-12.1
$\bar{5}$13	37.5	30.1
$\bar{5}$23	55.3	47.6
$\bar{5}$33	26.3	-25.9
$\bar{5}$43	36.2	32.9
$\bar{5}$53	25.2	22.9
$\bar{5}$63	9.3	8.8
$\bar{5}$73	26.8	-34.0
$\bar{5}$83	18.3	-20.4
$\bar{5}$93	8.4	11.1
$\bar{5}$,10,3	6.3	-13.3
$\bar{6}$13	22.1	-20.6
$\bar{6}$23	3.7	4.4+
$\bar{6}$33	28.7	23.8
$\bar{6}$43	4.0	0.35+
$\bar{6}$53	4.1	-3.4+
$\bar{6}$63	18.2	25.2
$\bar{6}$73	3.9	-5.3+
$\bar{6}$83	22.6	24.1
$\bar{6}$93	13.3	11.9
$\bar{6}$,10,3	10.8	-12.7
$\bar{7}$13	15.9	10.9
$\bar{7}$23	7.1	-8.1
$\bar{7}$33	10.0	-7.0
$\bar{7}$43	53.7	-53.4
$\bar{7}$53	4.0	-1.2+
$\bar{7}$63	20.9	18.6
$\bar{7}$73	14.6	-14.0
$\bar{8}$13	18.8	-19.8
$\bar{8}$23	4.1	5.8+
$\bar{8}$33	33.4	34.7
$\bar{8}$43	3.9	-7.3+
$\bar{8}$53	3.8	1.2+
$\bar{8}$63	21.5	-21.7
$\bar{8}$73	11.8	-9.4
$\bar{8}$83	11.7	-14.7
$\bar{9}$13	23.8	-27.2
$\bar{9}$23	17.6	23.4
$\bar{9}$33	12.0	11.3
$\bar{9}$43	3.8	-1.4+
$\bar{9}$53	3.6	-2.1+
$\bar{9}$63	11.6	12.8
$\bar{9}$73	17.7	23.6
$\bar{9}$83	9.6	-15.5
$\overline{10}$,1,3	13.8	-14.6
$\overline{10}$.2.3	21.1	-25.0
$\overline{10}$,3,3	18.1	-20.1
$\overline{10}$,4,3	11.9	15.2
$\overline{10}$,5,3	10.8	-14.8
$\overline{10}$,6,3	8.2	9.2
$\overline{11}$,1,3	6.4	11.0
$\overline{11}$,2,3	2.9	-7.3+
$\overline{11}$,3,3	12.0	16.0
$\overline{11}$,4,3	2.4	0.8+
$\overline{11}$,5,3	11.7	-22.9

this could be obtained from a difference synthesis down [001]. This was accordingly computed on the Stantec Zebra computer in our laboratory, using a programme due to Smits & Schoone (1959). The results are shown in Fig. 3. It is clear that the molecule is vibrating torsionally approximately about the normal to its plane. No attempt has been made to estimate vibration amplitudes from the difference map. The difference map also shows peaks of height about 2 e.Å^{-2} close to the positions of the hydrogen atoms bonded to C 3 and C 3′. In previous work (summarized by McDonald, 1956) peak heights of hydrogen atoms in projection have been found to be about 1 e.Å^{-2}, and it is therefore probable that appreciable contributions to these peaks do not come from the hydrogens.

(6) *Molecular dimensions*

The molecular dimensions calculated from the atomic positions are given in Fig. 4(*a*). The standard deviations of the atomic parameters were calculated in the usual way from the least-squares results and are given in Table 4. The best plane through the final atomic coordinates (Table 1) was found by minimizing

$$u = \sum_{i=1}^{N} w_i (ax_i' + by_i + cz_i')^2 / (a^2 + b^2 + c^2)\ ,$$

where the approximate relative weights w_i are given by

$$[\sigma_i(x)^2 + \sigma_i(y)^2 + \sigma_i(z)^2]^{-1}$$

because

$$\sigma_i(x) \approx \sigma_i(y) \approx \sigma_i(z)\ .$$

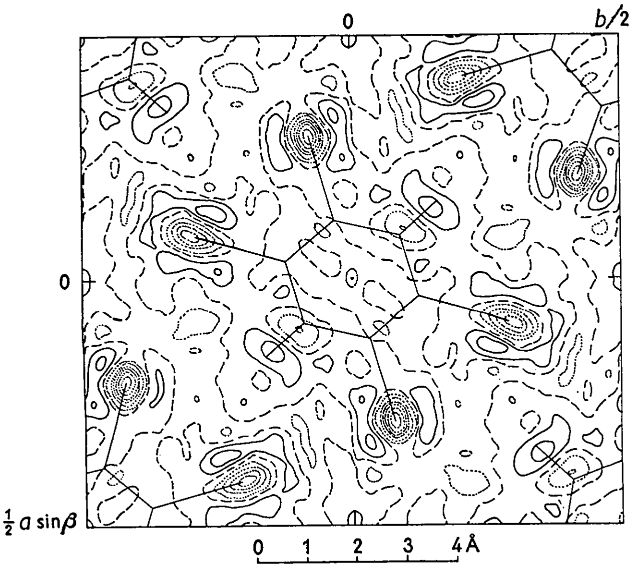

Fig. 3. Difference synthesis projected down [001]. Contours at intervals of 1 e.Å^{-2}, zero contour dashed and negative contours dotted. The atomic positions obtained from the three-dimensional least-squares analysis are shown on the projection.

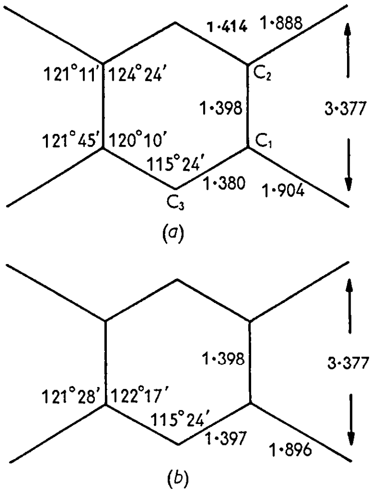

Fig. 4. Molecular dimensions: (a) experimental values, (b) averaged values, assuming molecular symmetry D_{2h}–*mmm*.

Table 3. *Perpendicular distances of atoms from best molecular plane*

Atom	Distance
Br 1	0·000 Å
Br 2	0·000
C 1	+0·031
C 2	−0·002
C 3	+0·003

x' and y are measured (in Å) along the [100] and [010] axes respectively, while the z' axis is perpendicular to both [100] and [010] axes. The equation to the molecular plane is

$$0{\cdot}56297x' - 0{\cdot}19664y - 0{\cdot}80274z' = 0\ .$$

The perpendicular distances of the atoms from this plane are given in Table 3.

Within the accuracy of the measurements the molecular symmetry is D_{2h}–*mmm*. The averaged dimensions are given in Fig. 4(*b*); the standard deviations of the mean dimensions are:

$\sigma_m(\text{Br}\cdots\text{Br}) = 0{\cdot}004$ Å

$\sigma_m(\text{C–C}) = 0{\cdot}026$ Å

$\sigma_m(\text{C}\hat{\text{C}}\text{C}) = 2°\,24'$.

$\sigma_m(\text{C–Br}) = 0{\cdot}018$ Å

$\sigma_m(\text{C}\hat{\text{C}}\text{Br}) = 1°\,9'$

Only one deviation from a regular planar model has been established with certainty: if all angles were 120°, C–C = 1·398 Å, C–Br = 1·896 Å, then Br ··· Br would be 3·294 Å. The distance found is 3·377 Å and $\Delta l/\sigma \approx 21$. This difference is very highly significant.

Table 4. *Standard deviations of the atomic parameters*

Atom	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$	$\sigma(B)$
Br 1	0·0027 Å	0·0028 Å	0·0032 Å	0·046 Å^2
Br 2	0·0026	0·0027	0·0030	0·045
C 1	0·026	0·026	0·030	0·42
C 2	0·023	0·024	0·027	0·38
C 3	0·025	0·025	0·030	0·44

None of the other deviations from the values used for the regular model is significant and thus no information has been obtained about possible distortions of the benzene ring.

3. Molecular structure

(1) *Discussion of molecular dimensions*

(i) C–Br *bond lengths*.—The mean C–Br distance in 1:2-4:5-tetrabromobenzene is 1·896 ± 0·018 Å, while the mean C–Br distance in polyhalogenated methanes is 1·937 ± 0·003 Å (*Tables of Interatomic Distances*, 1958). The difference is significant. The value obtained here for tetrabromobenzene is close to the average (loc. cit.) for C–Br bonds in olefinic compounds (1·89 ± 0·01 Å), and is larger than that given for aromatic C–Br bonds (1·85 ± 0·01 Å). However, very accurate experimental values were not available for deducing the averages for olefinic and aromatic compounds and the discrepancy is of doubtful significance. Our present result is in general agreement with previous conclusions (Pauling, 1939) that carbon–halogen bond-lengths are shorter in conjugated or aromatic molecules than in non-conjugated systems. Current opinion (Bersohn, 1954; Howe & Goldstein, 1957) is that this shortening is to be ascribed mainly to the smaller effective radius of the carbon atom in the sp^2 state as compared to that in the sp^3 state, and that the amount of double-bond character in the carbon–halogen bonds is only a few per cent rather than the 15–20% assumed previously (Sherman & Ketelaar, 1939).

(ii) *Distance between non-bonded bromine atoms.*—The intramolecular Br · · · Br distance of 3·377 ± 0·004 Å is about 0·4 Å less than the usual value given for the van der Waals separation of bromine atoms in different molecules (3·8 Å, see Pauling, 1939). As bond-stretching force constants are larger than angle-bending force constants, it seems probable that the increase of 1° 28′ found in the C–C–Br angles is a real effect, even though not statistically significant. Dean, Pollak, Craven & Jeffrey (1958) found, in 1:2-4:5-tetrachlorobenzene, that the angle between C–Cl vectors was 63 ± 1°. Although Dean *et al.* (1958) discuss this increase as being consistent with a non-planar molecule, it can better be considered as demonstrating an increase in C–C–Cl angles by $1\frac{1}{2}$°, with the same sort of in-plane splaying-out of C–Cl bonds as is found in the bromo-compound.

The equilibrium configuration of molecules of this type can be calculated for comparison with experiment. This has been done for the symmetrical tetrachloro-, tetrabromo- and tetraiodobenzenes as follows. It is assumed that the molecule remains planar and that the overcrowding of adjacent halogen atoms is relieved by splaying-out of the C-halogen bonds in the plane of the molecule. The absolute molecular steric energy is made up of two contributions:

(*a*) The angle strain energy due to an increase of the C–C–X bond angles beyond 120°. Because of the symmetry of the molecules, C–C–H angles will not be changed by splaying-out of the C–X bonds. Thus the angle strain energy is zero for $C\hat{C}X = 120°$, and is always positive.

(*b*) The van der Waals interaction between pairs of adjacent atoms. Here the interaction energy is taken to be zero at infinite atomic separation, and may be negative or positive according to the shapes of the van der Waals curves and the interatomic distances involved.

The angle strain energy per molecule is calculated from:

$$E_1 = \tfrac{2}{3}(k_X/r^2_{CX})(\Delta R_{XX})^2,$$

where k_X is the bending force constant of the CCX bond angle and ΔR_{XX} is the increase in the distance between adjacent halogen atoms. The values of the bending force constants used are as follows:

$C\hat{C}Cl$: $k_{Cl} = 1{\cdot}21 \times 10^{-11}$ ergs rad^{-2} (estimated from two following values).

$C\hat{C}Br$: $k_{Br} = 1{\cdot}07 \times 10^{-11}$ ergs rad^{-2} (Westheimer, 1947).

$C\hat{C}I$: $k_I = 0{\cdot}93 \times 10^{-11}$ ergs rad^{-2} (Rieger & Westheimer, 1950).

The van der Waals interaction energy per molecule is given by:

$$E_2 = 2E_{XX}(R) + 4E_{XH}(R),$$

where $E_{XX}(R)$ is the van der Waals interaction energy of two halogen atoms a distance R_{XX} apart, and $E_{XH}(R)$ is the interaction energy of a halogen and hydrogen atom separated by R_{XH}. The functions used for determining the van der Waals interaction energies are given in Table 5. Data for chlorine–chlorine interactions were determined by Morino & Miyagawa (1947) from the second virial coefficient of Cl_2 gas, while the other expressions were estimated by Hill (1948*a*) and Rieger & Westheimer (1950) on

Table 5. *Van der Waals interaction functions*

The interaction energy $E(R)$ is given by the equation

$$E(R) = a/R^{12} - b/R^6.$$

The constants listed give $E(R)$ in ergs/atom pair when R is in Å.

Interaction between	a erg Å^{12}	b erg Å^6	Reference
Cl · · · Cl	$1{\cdot}620 \times 10^{-7}$	$1{\cdot}515 \times 10^{-10}$	(*a*)
	$1{\cdot}435 \times 10^{-7}$	$1{\cdot}119 \times 10^{-10}$	(*b*)
Cl · · · H	$5{\cdot}171 \times 10^{-9}$	$1{\cdot}284 \times 10^{-11}$	(*b*)
Br · · · Br	$3{\cdot}792 \times 10^{-7}$	$2{\cdot}155 \times 10^{-10}$	(*b*)
Br · · · H	$9{\cdot}005 \times 10^{-9}$	$1{\cdot}844 \times 10^{-11}$	(*b*)
I · · · I	$1{\cdot}728 \times 10^{-6}$	$5{\cdot}475 \times 10^{-10}$	(*c*)
I · · · H	$1{\cdot}570 \times 10^{-8}$	$2{\cdot}616 \times 10^{-11}$	(*c*)

(*a*) Morino & Miyagawa (1947).
(*b*) Hill (1948*a*).
(*c*) Rieger & Westheimer (1950).

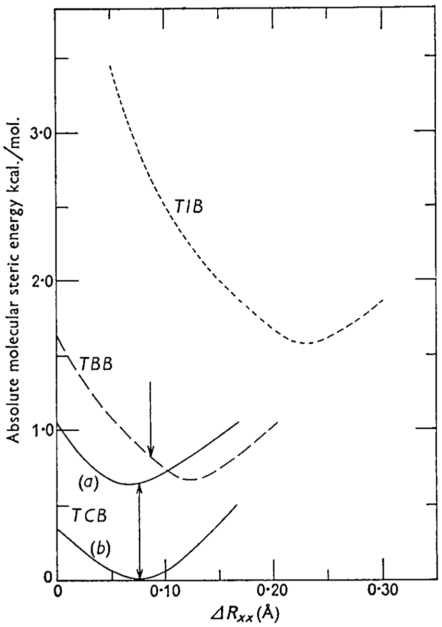

Fig. 5. Variation of absolute molecular steric energy (in kcal/mole) with increase in distance between adjacent halogen atoms for:

TCB: 1:2-4:5-tetrachlorobenzene (*a*) using Hill's (1948*a*) form of the van der Waals interaction energy, (*b*) using the function given by Morino & Miyagawa (1947). TBB: 1:2-4:5-tetrabromobenzene. TIB: 1:2-4:5-tetraiodobenzene. Calculated values of ΔR_{XX} are given by the minima of the curves, while the experimental values are shown by arrows.

plausible grounds. It should, however, be emphasized that although the adjustable parameters have been chosen to give agreement with known van der Waals radii, the theoretical basis for these expressions is not well-established.

The total energy is given by E_1+E_2, and is most conveniently obtained using graphs of $E_{XX}(R)$ and $E_{XH}(R)$. From the geometry of the molecules, it can easily be shown that $\Delta R_{XH} = -0{\cdot}4\Delta R_{XX}$. The curves obtained are shown in Fig. 5. It will be seen that for 1:2-4:5-tetrachlorobenzene good agreement with experiment is obtained for both potential functions. For 1:2-4:5-tetrabromobenzene the calculated value of ΔR_{BrBr} is about 50% larger than the experimental value. For 1:2-4:5-tetraiodobenzene the calculated value of ΔR_{II} is 0·23 Å, but no experimental value is available for comparison. There are not yet sufficient results available for one to judge whether the potential functions used, which were developed for intermolecular approaches, are also adequate for intramolecular approaches. It is possible that a variation of the van der Waals function with angle from the covalent bond should be introduced, as suggested by Pauling (1939) and Dostrovsky, Hughes & Ingold (1946).

The calculation carried out above is a simplified version of the methods introduced by Westheimer & Mayer (1946) and Hill (1948*b*). The simplifications are neglect of angle bending within the benzene ring and of the possibility of changing the lengths of any of the bonds of the molecule. Inclusion of these effects would produce only small changes in the values of ΔR_{XX} calculated above.

It would be desirable to carry out a parallel calculation for the model proposed by Bastiansen & Hassel (1947) from their electron-diffraction results but unfortunately the force constants for out-of-plane bending of C-halogen bonds are lacking. However, on qualitative grounds this model seems very unlikely as an out-of-plane bending of $\pm 14°$ would be required to increase the Br · · · Br distance to 3·38 Å, as compared to an in-plane bending of only $\pm 1\frac{1}{2}°$.

(2) *Comparison with nuclear quadrupole resonance data*

The variations in nuclear quadrupole resonance frequencies in the various polyhalogenated benzenes in the solid state have been discussed by Duchesne & Monfils (1954), Bray, Barnes & Bersohn (1956) and Cassabella, Bray, Segel & Barnes (1956). Duchesne & Monfils based their theory on the presumed non-planarity of molecules containing ortho halogen atoms; as these molecules are planar, this theory must be rejected. Bray, Barnes and co-workers explain the increase in resonance frequency with number of halogens on the ring in terms of an inductive effect, which decreases the ionic character of the bonds around the ring. Although these authors assume non-planarity of the molecules, they point out that deviations from planarity would only have minor effects on the resonance frequencies.

(3) *Planarity of polyhalogenated benzenes*

The molecular structures of polyhalogenated benzenes containing halogen atoms bonded to adjacent carbon atoms have been uncertain for some time. The situation has been complicated by differing results reported by various authors and by apparent differences between molecular conformations in the solid and fluid phases.

Recent results, including those reported here, enable one to draw firm conclusions regarding the conformations in the solid state but the situation for molecules in the liquid or vapour states is still uncertain.

The present results show that 1:2-4:5-tetrabromobenzene is planar and from the isomorphism of the room temperature (β) phases of 1:2-4:5-tetrabromo- and tetrachlorobenzenes we can infer that the latter is also planar. The similarity of molecular volumes in polymorphs of these two compounds suggests that it is the molecular arrangements, and not their shapes, which differ in the various polymorphs.

An early and incomplete analysis of the crystal structure of hexachlorobenzene (Lonsdale, 1931) indicated that the molecule was planar. A similar conclusion was reached by Tulinsky & White (1958) on the basis of two-dimensional projections down the short [010] axis. The infra-red spectra of crystals and solutions between 2–15μ have also been tentatively interpreted in terms of a planar molecule (Kopelman & Schnepp, 1959). However, the same authors have suggested, from an analysis of the ultra-violet spectrum of crystalline hexachlorobenzene, that the molecule may well be puckered (Schnepp & Kopelman, 1959). As the crystallographic results are less liable to misinterpretation than the spectroscopic results, we conclude that it is most probable that hexachlorobenzene is planar in the solid state. As hexabromobenzene is isomorphous with hexachlorobenzene (Plummer, 1925; Gafner & Herbstein, 1960) it too will be planar.

From the evidence given above we conclude that polychlorinated and polybrominated benzenes containing halogens ortho to one another are planar in the solid state despite the close approach distances between the ortho halogen atoms. No comparable fluorine or iodine derivatives have yet been examined experimentally. It should be noted that none of the experimental work cited above was accurate enough to detect small deviations from planarity of 0·01–0·02 Å. Deviations from planarity of this magnitude have recently been found in anthracene (Cruickshank, 1956) and α-phenazine (Hirshfeld & Schmidt, 1957) and have been ascribed to packing effects.

In the liquid and vapour states the evidence regarding the molecular structures is confused. The electron-diffraction results of Brockway & Palmer (1937) for seven polychlorobenzenes (including *o*-dichlorobenzene, 1:2-4:5-tetrachlorobenzene and hexachlorobenzene) were interpreted in terms of planar molecules, with a small in-plane splaying apart of adjacent chlorine atoms in those molecules where this is possible. A later sector electron-diffraction investigation of similar compounds (including *o*-dichloro and dibromobenzene, 1:2:3-5-tetrabromobenzene, hexachlorobenzene and hexabromobenzene) by Bastiansen & Hassel (1947) led to the conclusion that these molecules were non-planar, with adjacent halogen atoms bent alternately above and below the benzene-ring plane. For the *o*-dihalogen compounds the angle of bending was ± 18°. There is some evidence from the ultra-violet spectrum of 1:2-4:5-tetrachlorbenzene vapour (Matubara & Anno, 1956) that the molecule is non-planar in one or both of its electronic states, but the assignment of the vibrations cannot be taken as conclusive. Contrary conclusions have been drawn from the infrared and Raman spectra of 1:2-4:5-tetrafluorobenzene (Ferguson, Hudson, Nielsen & Smith, 1953) and hexafluorobenzene (Delbouille, 1956; Steele & Whiffen, 1959), planar molecules being indicated in both instances for the vapour and liquid states.

One possible explanation for the discrepancy between Bastiansen & Hassel's results and our present conclusion of planar molecular conformations in the crystals would be a change of conformation on vaporization. As mentioned previously (Harnik, Herbstein, Schmidt & Hirshfeld, 1954) this would imply that the packing forces in the crystals are large enough to compress the molecules into a planar shape; this seems inherently unlikely and a repetition of the electron-diffraction measurements is desirable.

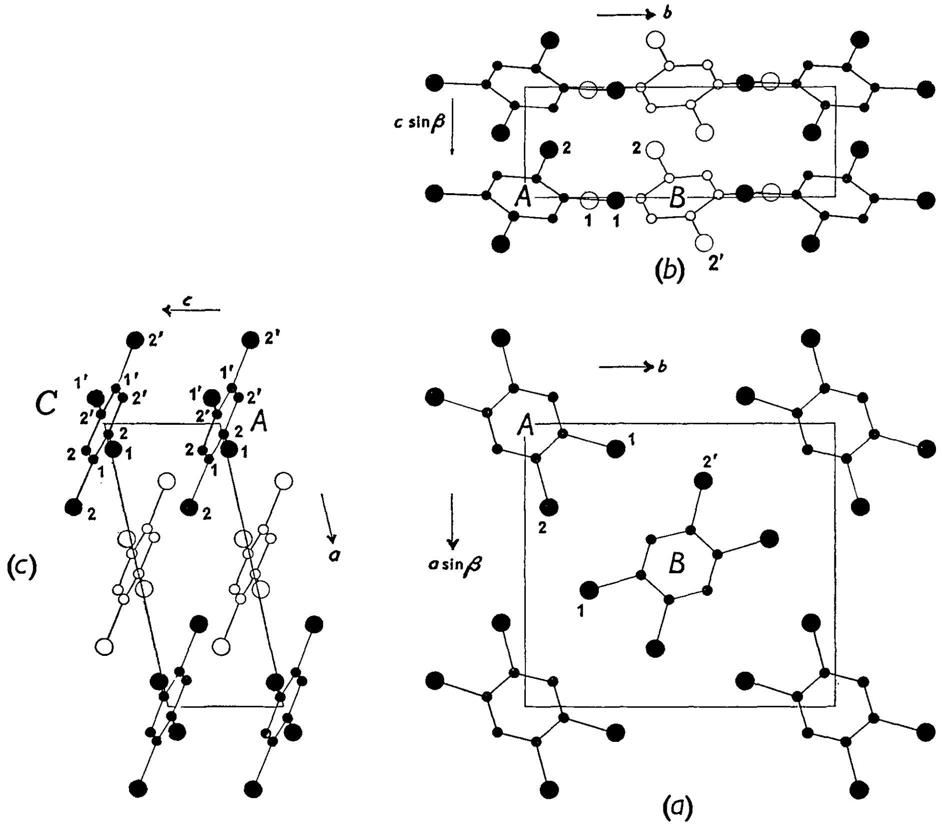

Fig. 6. Molecular arrangement.

(*a*) Projection of unit-cell contents down [001].

Shorter intermolecular distances (Å) between stacks.

	A	*B*		
Br	2	1	4·10	
	1	2′	4·85	
	1	H	3·18	(postulated hydrogen position used).

(*b*) Projection of unit-cell contents down [100].

(*c*) Projection of unit-cell contents down [010].

Shorter intermolecular distances within a stack.

A	*C*	
Br 1	Br 1	4·02 Å
Br 2	Br 1	4·08
Br 2	Br 2	4·02
Br 2	C 1	3·81
Br 2	C 2	3·87
C 1	C 2	3·72
C 3	C 1′	3·76
C 2′	C 1′	3·72
C 2	C 3′	3·80

4. Crystal structure

(1) *Molecular arrangement*

The packing of the molecules in the crystal is shown in Fig. 6(*a*), (*b*), (*c*). The molecules are arranged in stacks along the [001] directions, each stack being immediately surrounded by four others. The stack at $[[\frac{1}{2}, \frac{1}{2}, -]]$ is derived from that at $[[0, 0, -]]$ by the action of the *a* glide plane; the angle between the molecular planes in the two stacks is 22° 33′. Within any one stack the molecules are parallel, with an interplanar distance of 3·64 Å. However, the superposed molecules are staggered to prevent direct overlap of the atoms (Fig. 7) and the actual interatomic distances are all larger than the nominal van der Waals distances. The shorter intermolecular distances are given with Fig. 6. The packing of the stacks is comparatively loose and close contacts occur only between a bromine of one molecule and a hydrogen of another. On the assumption of a plausible position for the hydrogen atom, the distance between Br 1_A and H_B is 3·18 Å, somewhat larger than the sum of the respective van der Waals radii ($1{\cdot}9+1{\cdot}2 = 3{\cdot}1$ Å). The shortest Br ··· Br distance found between stacks is 4·10 Å (Br 2_A ··· Br 1_B).

The molecules are arranged so that the number of close approaches between bromine atoms of neighbouring molecules is minimized, possibly as a consequence of repulsion between C–Br dipoles. The interaction between C–Br and C–H dipoles is less important because of the small C–H bond moment; in aromatic compounds the positive charge of the C–H dipole is probably on the hydrogen atom (Coulson, 1952) and the interaction will be attractive. The molecular arrangement projected down [001] has pseudo-fourfold symmetry compared to the pseudo-sixfold symmetry found, for example, in the [010] projection of hexachlorobenzene. A striking difference between the crystal structures of hexachlorobenzene and *β*-sym.-tetrabromobenzene is that the stacks are approximately hexagonally close-packed in the former but not in the latter. The crystal structures of the four geometrically-similar molecules—1:2-4:5-tetrachlorobenzene, 1:2-4:5-tetrabromobenzene, durene (1:2-4:5-tetramethylbenzene) (Robertson, 1933) and tetramethylpyrazine (Cromer, Ihde & Ritter, 1951)—are known. The molecular arrangement in the isomorphous *β*-phases of the first two compounds is described above. In durene the molecules are also arranged in stacks but the 49° inclination of the molecular planes to (010) results in an overlap of only the methyl-group regions when two successive molecules in a stack are projected onto the molecular plane. Another difference between the two structures is that in durene the close approaches between neighbouring stacks are through methyl groups. In tetramethylpyrazine the structure can be described in terms of molecular layers: the arrangement of molecules in the (100) plane is very similar to that in the (001) plane of 1:2-4:5-tetrabromobenzene (see Fig. 6(*a*)), although the tetramethylpyrazine molecules are inclined at a rather greater angle to (100). The layer at $\frac{1}{2}a$ is related to that at $x=0$ by the action of the *b* glide plane at $\frac{1}{4}a$ (note $[100]=8{\cdot}35$ Å). There are no stacks of parallel molecules in the crystal. Two other molecules which have the same shape as each other but show differences in crystal structures are B,B,B-trichloroborazole and 1:3:5-trichlorobenzene (Lonsdale, 1959). These data show that determination of crystal structures by arguments based on similarity of molecular shapes or unit-cell dimensions (Brown, 1951) is not a procedure of general validity.

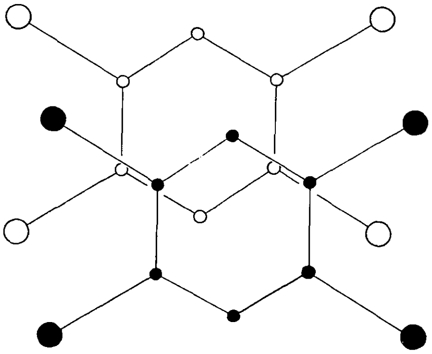

Fig. 7. Normal projection of two molecules in the same stack separated by unit translation along [001].

The only faces found on the *β*-tetrabromobenzene crystals were {110} and reference to Fig. 6(*a*) shows that these planes are the most densely populated.

(2) *Twinning*

Many contact twins and occasional lamellar twins were found among the crystals of *β*-1:2-4:5-tetrabromobenzene and *β* - 1:2 - 4:5 - tetrachlorobenzene grown from solution. Although some twin formation in the former may be due to $\gamma \rightarrow \beta$ transformations occurring in *γ*-phase crystals cooled below 46 °C. (Johnson, 1956) a large proportion of the twins found must be true growth twins as they are also found in crystals grown by evaporation of solutions held at room temperature. The twinning in *β*-1:2-4:5-tetrachlorobenzene (also reported by Dean *et al.*, 1958) cannot be transformation twinning as no high-temperature phase appears in this compound (Gafner & Herbstein, 1960).

Zero and first-level equi-inclination Weissenberg photographs of a twinned crystal show that the [001] axes of the two individuals are parallel and the twin planes are respectively (110) and $(\bar{1}10)$. An alternative but equivalent description is with the [001] axes of the two individuals antiparallel, the twin planes now being (110) for both individuals.

In terms of Friedel's classification of twins (Cahn, 1954) the crystals are reflexion twinned by pseudo-merohedry, [110] being a pseudo-twofold axis. The obliquity of the twins, defined as the angle between

[110] and the normal to the (110) planes is 11° 8′ for β-1:2-4:5-tetrachlorobenzene, and 9° 16′ for β-1:2-4:5-tetrabromobenzene. In both crystals the obliquities are considerably larger than the values usually found.

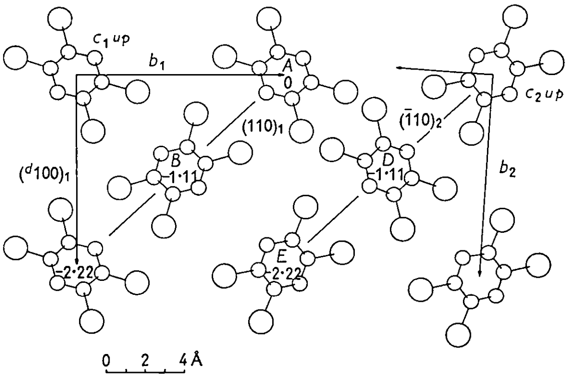

Fig. 8. Molecular arrangement in twinned crystals (see text for explanation). The distances (Å) of molecular centres below the plane of the paper are given together with the molecular designations.

The molecular arrangement in the twinned crystals is illustrated in Fig. 8, where projections down [001] are shown of two individuals with the relative orientation

$$[001]_1 \parallel [001]_2; \quad (110)_1 \parallel (\bar{1}10)_2 \text{ deduced above.}$$

If the molecular positions in the twin boundary are a compromise between those in corresponding stacks in $(110)_1$ and $(\bar{1}10)_2$ (i.e. *A* and *D*, *B* and *E* etc.) then the angle between the plane of a molecule in the twin boundary and that of a corresponding molecule in the untwinned crystal will be $8\frac{3}{4}$°. This arrangement can be accomplished geometrically by shifting origin 2 by $\frac{1}{2}(\mathbf{a}_1+\mathbf{b}_1)$ from initial coincidence with origin 1, and allowing small changes in molecular orientations. The resulting changes in nearest-neighbour distances in the vicinity of the twin boundary will be small, as will the associated energy. It is nevertheless interesting to note that the boundaries can be seen quite clearly by unpolarized light in transmission when the twin plane makes an angle of a few degrees with the light beam.

We are grateful to Dr J. N. van Niekerk for his interest in this work.

Note added in proof.

After this paper was accepted for publication, some calculations of steric effects in halogenated benzenes were published by Coulson & Stoker (1959), and it is of interest to compare their conclusions with ours.

Coulson & Stocker show first that electrostatic forces, due to the dipolar nature of the C–X bonds, will not lead to buckling of C_6X_6 molecules. Then using Hill's (1948*a*) van der Waals functions for the interactions between non-bonded atoms, they conclude that only C_6I_6 will be buckled. No buckling is to be anticipated in any of the C_6X_6 molecules if the non-bonded interactions are estimated from exchange forces. These conclusions are in agreement with the experimental evidence for C_6Cl_6 and C_6Br_6 summarized above (Section **3**, 3); the structure of C_6I_6 has not been reported.

More controversial conclusions were obtained when an alternative method of determining the potential function for two non-bonded chlorine atoms was used. In this method Coulson & Stocker use the known potential function for CCl_4 molecules in the gas phase (Hirschfelder, Curtiss & Bird, 1954) in order to derive an expression (their equation (8)) for the interaction energy which includes some allowances for polarity effects. Using this function they calculate that the chlorine atoms in C_6Cl_6 are alternately 0·33 Å above and below the mean molecular plane. A reduction of the interaction energies by a factor of two would reduce these out-of-plane displacements by a factor of about four, but even these are far too large to be reconciled with the experimental results of Tulinsky & White (1958).

Disagreement with experiment is also obtained for the ortho-disubstituted benzenes. For *o*-dichlorobenzene Coulson & Stocker calculate that the molecule should be planar but that $C\hat{C}Cl$ should be increased by 4°. (The method used for this calculation is the same as that given by us in Section **3**, 1(ii)). They then remark that 'in the case of the bromo-compound, the observed value of θ (the angular displacement) is $1\frac{1}{2}$° (Gafner & Herbstein, 1958) but the accuracy of this displacement is not sufficiently great to justify a comparison with the theoretical value.' In fact the true situation is just the contrary—the experimental value is far more reliable than the theoretical. It is to be expected that the value of θ in the bromo-compound will not be less than that in the corresponding chloro-compound. A value of $\theta = 4°$ would lead to $d(\mathrm{Br}\cdots\mathrm{Br}) = 3{\cdot}52$ Å, instead of the observed value of $3{\cdot}377 \pm 0{\cdot}004$ Å. Thus the results obtained on the basis of Coulson & Stocker's equation (8) for hexachlorobenzene and *o*-dibromobenzene lie far outside the limits of experimental error and we conclude that this expression for the interaction between non-bonded chlorine atoms (or an analogous one for bromines) is not acceptable. The potential functions given by Hill remain the best available in the literature.

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