

## Electron Diffraction Investigation of Gaseous Tetrabromoethylene and Hexabromobenzene

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The molecular structures of tetrabromoethylene and hexabromobenzene have been studied by the gas electron diffraction method. Tetrabromoethylene possesses  $D_{2h}$  symmetry with  $r_{C-C} = 1.362$  (0.009) Å,  $r_{C-Br} = 1.881$  (0.003) Å, and  $\angle BrCBr = 115.2$  (0.3)°. The *ortho* Br...Br distance in hexabromobenzene indicates that this molecule is distorted from a configuration with  $D_{6h}$  symmetry. Values for the bond distances are  $r_{C-C} = 1.403$  (0.005) Å and  $r_{C-Br} = 1.880$  (0.004) Å. Results using nonrelativistic partial waves atomic scattering factors based upon both a relativistic and a non-relativistic Hartree-Fock potential of bromine are given. Better agreement with the experimental data and more reasonable values for the C...Br amplitudes of vibration are obtained for the former scattering factors.

The failure of the first Born approximation to adequately describe the scattering of medium energy electrons from heavier atoms is well known.<sup>1,2</sup> With the aid of electronic computers accurate calculations of partial waves atomic electron scattering factors are now possible,<sup>3,4</sup> and the calculations can be based upon steadily improving values for the atomic potentials.

To see if improved electron scattering factors actually lead to improved structure parameters from electron diffraction experiments, tetrabromoethylene and hexabromobenzene have been studied using scattering factors calculated from both a relativistic and a nonrelativistic Hartree-Fock potential of bromine.

Both tetrabromoethylene and hexabromobenzene are overcrowded in the sense that the neighbouring Br...Br distances in undistorted models of the molecules are shorter than twice the van der Waals radius of bromine. In an earlier electron diffraction investigation of hexabromobenzene by the author,<sup>5</sup> the *ortho* Br...Br distance indicated that this molecule is distorted. However, the agreement between the experimental distances and the distances of the most likely models was not quite satisfactory, and additional experimental data have been collected for the present investigation.

In the  $C_2X_4$  molecules, it is of interest to study a possible variation of the C=C-bond for X=F, Cl, Br, and I. Tetrabromoethylene was included in this investigation because it is supposed to possess a simple symmetric structure, and the root mean-square amplitudes of vibration have been calculated from spectroscopic data.<sup>6</sup> The results might therefore indicate how accurate the distances can be determined for molecules with a high ratio of nonbonded Br...Br distances. Also, charge transfer compounds with tetrabromoethylene are currently being investigated at this institute,<sup>7</sup> and an accurate structure determination of the free molecule is of interest for this work.

### THEORY

The modified experimental molecular intensities,  $I_M^E(s_j)$ , are determined at the points  $s_j$  for the scattering parameter  $s$  defined by  $s = 2k \sin \theta$ , where  $\vec{k}$  is the wave vector for the electrons and  $2\theta$  is the scattering angle. To obtain these intensities, the intensities measured from the photographic plates are multiplied by the blackness correction, the correction for using planar photographic plates, the sector correction,  $s^4$ , and a modification function  $\varphi(s)$ . Furthermore, the experimental background has to be withdrawn from the corrected intensities to obtain  $I_M^E(s_j)$ . The corresponding modified theoretical intensities can then be written as

$$I_M^T(s) = k_s \frac{\varphi(s)}{s} \sum_{i=1}^N \frac{2n_i}{r_i} |f'_m| |f'_n| \cos(\eta_m - \eta_n) \exp(-\frac{1}{2} l_i^2 s^2) \sin sr_i \quad (1)$$

In eqn. 1,  $k_s$  is a scale factor because the experimental intensities are on an arbitrary scale,  $N$  is the total number of different distances in the molecule, and the distance  $r_i$  between the atoms  $m$  and  $n$  with a root mean-square amplitude of vibration  $l_i$ , repeats itself  $n_i$  times due to a possible symmetry of the molecule.  $|f'|$  and  $\eta$  are related to the complex atomic electron scattering factor  $f$  through the equation

$$|f'| \exp(i\eta) = \frac{as^2}{2} |f| \exp(i\eta) \quad (2)$$

where  $a$  is the first Bohr radius of hydrogen. The atomic electron scattering factors can be calculated from

$$f(\theta) = \frac{1}{2ik} \sum_{n=0}^{\infty} (2n+1) [\exp(2i\delta_n) - 1] P_n(\cos \theta) \quad (3)$$

The partial wave phase shifts  $\delta_n$  are obtainable as solutions of the proper radial Schrödinger equation with knowledge about the atomic potentials.<sup>1-4</sup> Through eqn. 3 the many body scattering problem is reduced to nonrelativistic scattering from a radial symmetric potential, so polarization and exchange effects are not included in the calculations.

Eqn. 1 is valid for kinematic scattering from the molecule and for independent harmonic vibrations between each pair of atoms. With the use of atomic scattering factors according to eqn. 3, effects from a perturbation of the atomic fields from the chemical bonds are not included.

The electron diffraction distance parameter  $r_i = r_i^g$  is for vibrations in the ground state of a Morse potential with asymmetry constant  $a$  related to the position for the minimum of the potential  $r^e$  through the equation

$$r^g \approx r^e - l^2/r^e + 3al^2/2 \quad (4)$$

and the expression for the molecular intensities is changed.<sup>8</sup> Setting  $a = 0$  in eqn. 4, the corresponding relation for a harmonic potential is obtained. However, the vibrations between pairs of atoms in polyatomic molecules usually represent complex combinations of the normal vibrations, and eqn. 4 is not generally valid, especially if the experimental nonbonded  $r^g$  distances also are expected to be in agreement with the distances calculated for a model of the molecule. That the former distances were shorter than the latter ones were first observed and explained by Bastiansen.<sup>9</sup> The theory was developed by Morino,<sup>10</sup> and the effect is often referred to as the Bastiansen-Morino shrinkage effect.

A radial distribution function for the molecule might be defined as

$$\frac{\sigma(r)}{r} = \int_{s_2}^{s_1} I_M(s) \exp(-ks^2) \sin sr \, ds \quad (5)$$

where  $\exp(-ks^2)$  is an artificial damping function to take care of the outer termination error of the integral. By choosing the modification function  $\varphi(s)$  as

$$\varphi(s) = \frac{s}{|f'|_k |f'|_l} \quad (6)$$

the contribution to the radial distribution function from one type of distances in a molecule might be made Gaussian by a proper choice of  $k$  and  $l$  and by taking care of the inner termination error of the integral. The  $r_i$ 's and  $l_i$ 's might be obtained from the experimental radial distribution function, but the structure parameters can also be determined by solving the set of nonlinear simultaneous equations resulting from the least squares criterium

$$\sum_j w_j \Delta_j^2 = \sum_j w_j [I_M^E(s_j) - I_M^T(k_s, r_i, l_i, s_j)]^2 = \min \quad (7)$$

where  $w$  is a weighting function.

For a modification function of eqn. 6 it is convenient to define the functions

$$g_{mn} = \frac{|f'|_m |f'|_n}{|f'|_k |f'|_l} \cos(\eta_m - \eta_n) \quad (8)$$

and eqn. 1 can then be written as

$$I_M^T(s) = k_s \sum_{i=1}^N \frac{2n_i}{r_i} g_{mn} \exp(-\frac{1}{2}l_i^2 s^2) \sin sr_i \quad (9)$$

It should also be mentioned that the form of  $f'$  of eqn. 2 has been chosen because in the first Born approximation.

$$|f'| = Z - F \text{ and } \eta = 0 \quad (10)$$

where  $F$  is the atomic X-ray scattering factor and  $Z$  is the atomic number.

## STRUCTURE INVESTIGATIONS

The experimental data for tetrabromoethylene were collected on the Oslo electron diffraction unit for an accelerating voltage of about 35 keV and for camera distances of about 48 and 19 cm. Treating the data the usual way,<sup>11</sup> average intensities from four plates for each camera distance from  $s = 1.75$  to  $s = 34.00$  in intervals of  $\Delta s = 0.25 \text{ \AA}^{-1}$  were obtained. In the region  $s = 10.00$  to  $s = 16.00 \text{ \AA}^{-1}$  the average intensities from the two camera distances were applied. The nozzle temperature was  $85^\circ\text{C}$ .

The four additional plates for hexabromobenzene were from the new electron diffraction unit<sup>12</sup> for a camera distance of about 130 cm. The intensities for hexabromobenzene were four single curves and the average of these curves. Each single curve consisted of data from one plate from each of the three camera distances, with intensities from  $s = 1.00$  to  $s = 5.50$  for  $\Delta s = 0.125 \text{ \AA}^{-1}$  from the new 130 cm plates, and from  $s = 5.75$  to  $s = 29.00$  for  $\Delta s = 0.25 \text{ \AA}^{-1}$  from the plates of the earlier investigation.<sup>5</sup> The average intensities from the old 48 and 19 cm plates were applied between  $s = 9.25$  and  $s = 18.00 \text{ \AA}^{-1}$ . The nozzle temperature was  $200^\circ\text{C}$ .

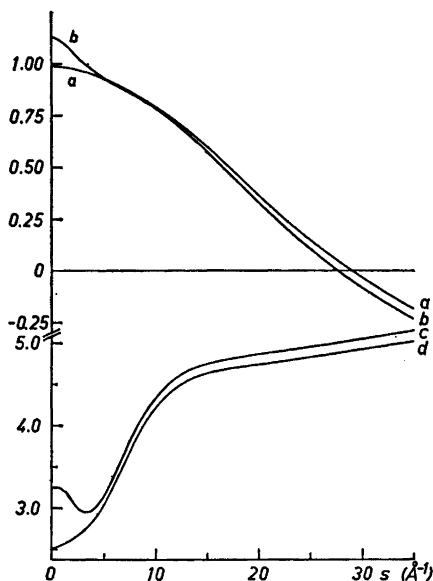


Fig. 1.  $g_{mn}$  functions of eqn. 8 for a modification function according to eqn. 11.

$$\begin{aligned} \text{a: } g_{mn} &= \cos(\eta_{\text{Br}}^{\text{R}} - \eta_{\text{C}}), \\ \text{b: } g_{mn} &= |f'_{\text{Br}}|^{\text{N}} \cos(\eta_{\text{Br}}^{\text{N}} - \eta_{\text{C}}) / |f'_{\text{Br}}|^{\text{R}}, \\ \text{c: } g_{mn} &= |f'_{\text{Br}}|^{\text{N}^2} / (|f'_{\text{C}}| \cdot |f'_{\text{Br}}|^{\text{R}}), \\ \text{d: } g_{mn} &= |f'_{\text{Br}}|^{\text{R}} / |f'_{\text{C}}|. \end{aligned}$$

R and N designate scattering factors and phases from a relativistic and nonrelativistic bromine potential, respectively.

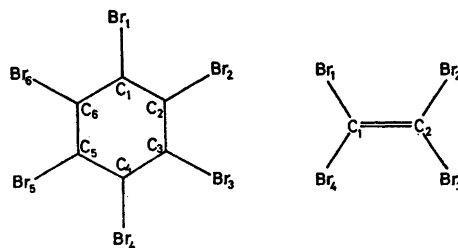


Fig. 2. Numbering of the atoms in hexabromobenzene and tetrabromoethylene.

Nonrelativistic atomic scattering factors for 35 keV electrons were computed according to eqn. 3.<sup>4</sup> For carbon, the calculations were based upon an analytical expression for the Hartree-Fock potential,<sup>13</sup> and for bromine upon both a nonrelativistic<sup>13</sup> and relativistic<sup>14</sup> potential. The expression for the relativistic potential of bromine of Ref. 14 was obtained by least squares fit to the relativistic Hartree-Fock-Slater radial density for bromine<sup>15</sup> with an improved exchange approximation.<sup>16</sup>

The tetrabromoethylene data were modified with the function

$$\varphi(s) = \frac{s}{|f'|_c |f'|_{\text{Br}^{\text{R}}}} \quad (11)$$

and the hexabromobenzene data with

$$\varphi(s) = \frac{s}{|f'|_c |f'|_{\text{Br}^{\text{N}}}} \quad (12)$$

where  $|f'|_{\text{Br}^{\text{N}}}$  and  $|f'|_{\text{Br}^{\text{R}}}$  are nonrelativistic scattering factors for bromine for the nonrelativistic and relativistic potential, respectively. The  $g_{mn}$  functions of eqn. 8 were computed for the two bromine scattering factors. The two sets of  $g_{mn}$  functions for a modification function of eqn. 11 are illustrated in Fig. 1.

The molecular intensities were determined by withdrawing an experimental background and the structure parameters were determined by the least squares method according to eqn. 7. The backgrounds were then adjusted from the results of the first calculations until further adjustments did not improve the agreement between the experimental and the calculated intensities. The final results of different least squares iterations are given in Table 1 for tetra-

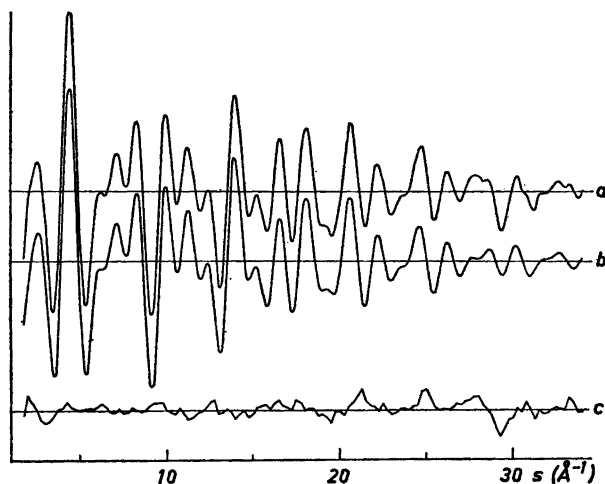


Fig. 3. Molecular intensities for tetrabromoethylene.

a:  $I_{\text{M}}^{\text{E}}(s)$ , b:  $I_{\text{M}}^{\text{T}}(s)$ , c:  $I_{\text{M}}^{\text{E}} - I_{\text{M}}^{\text{T}}$ .  $I_{\text{M}}^{\text{T}}$  is calculated according to eqn. 9 with parameters from Table 1, f.

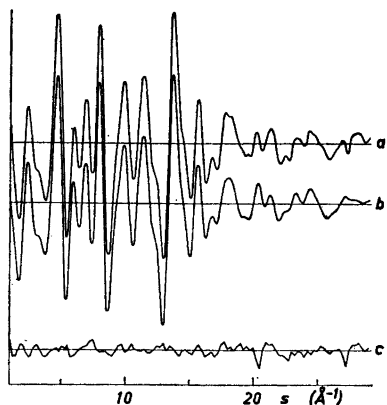


Fig. 4. Molecular intensities for hexabromobenzene.

a:  $I_M^E(s)$ , b:  $I_M^T(s)$ , c:  $I_M^E - I_M^T$ .  $I_M^T$  is calculated according to eqn. 9 with parameters from Table 2, f.

bromoethylene and in Tables 2 and 3 for hexabromobenzene. The results in the tables represent stable minima where further iterations do not change the parameters, and the standard deviations given do not include the contribution from systematic errors or from a possible correlation of the errors in the data. The numbering of the atoms in the molecules are illustrated in Fig. 2, the molecular intensity curves in Figs. 3 and 4, and radial distribution functions in Figs. 5 and 6.

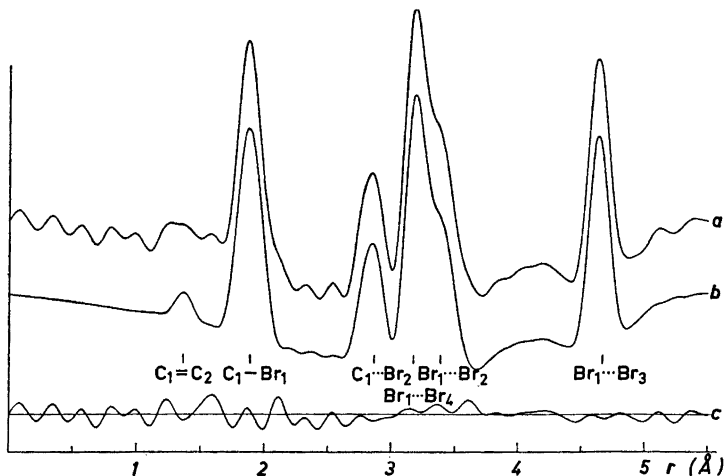


Fig. 5. Radial distribution functions for tetrabromoethylene according to eqn. 5. A damping function of  $\exp(-0.0009 s^2)$  was applied. a: From experimental molecular intensities. b: From theoretical molecular intensities with parameters of Table 1, f. c: Difference.

Table 1. Least squares results for the structure parameters of tetrabromoethylene.

a	b	c	d/e	f	g	h	i
$r_{C_1-C_2}$	1.3623(0.0056)	1.3691(0.0057)	[1.3623]	[1.3623]	[1.3623]	[1.3623]	[1.3623]
$r_{C_1-Br_1}$	1.8808(0.0016)	1.8824(0.0016)	1.8798(0.0022)	1.8800(0.0023)	1.8834(0.0031)	1.8782(0.0039)	1.8782(0.0039)
$r_{C_1 \cdots Br_2}$	2.8536	2.8564	2.8538(0.0037)	2.8528(0.0036)	2.8506(0.0054)	2.8503(0.0071)	2.8503(0.0071)
$r_{Br_1 \cdots Br_4}$	3.1763(0.0014)	3.1748(0.0014)	3.1738(0.0019)	3.1736(0.0019)	3.1724(0.0027)	3.1721(0.0026)	3.1721(0.0026)
$r_{Br_1 \cdots Br_2}$	3.3807	3.3819	3.3794(0.0036)	3.3797(0.0036)	3.3815(0.0043)	3.3710(0.0050)	3.3710(0.0050)
$r_{Br_1 \cdots Br_3}$	4.6373	4.6360	4.6381(0.0020)	4.6379(0.0020)	4.6374(0.0026)	4.6365(0.0024)	4.6365(0.0024)
$l_{C_1-C_2}$	[0.0430]	[0.0430]	0.0430	[0.0430]	[0.0430]	[0.0430]	[0.0430]
$l_{C_1-Br_1}$	0.0425(0.0043)	0.0428(0.0043)	0.0499	0.0422(0.0044)	0.0342(0.0054)	0.0499	0.0499
$l_{C_1 \cdots Br_2}$	0.0449(0.0060)	0.0463(0.0061)	0.0599	0.0444(0.0064)	0.0338(0.0082)	0.0599	0.0599
$l_{Br_1 \cdots Br_4}$	0.0744(0.0018)	0.0740(0.0019)	0.0711	0.0743(0.0019)	0.0746(0.0020)	0.0711	0.0711
$l_{Br_1 \cdots Br_2}$	0.1070(0.0028)	0.1067(0.0028)	0.0978	0.1068(0.0029)	0.1073(0.0029)	0.0978	0.0978
$l_{Br_1 \cdots Br_3}$	0.0699(0.0019)	0.0700(0.0020)	0.0606	0.0698(0.0020)	0.0696(0.0020)	0.0606	0.0606
$l_{BrUBr}$	115.2(0.1)	115.2(0.1)					
$k_s$	100.9(1.6)	101.0(1.6)	100.6(1.7)	97.6(1.6)	2.44(0.04)	12.5(0.3)	12.5(0.3)
$\sum wA^2 \times 10^{-5}$	1.64	1.69	1.63	1.64	$8.27 \times 10^{-4}$	$5.03 \times 10^{-2}$	$5.03 \times 10^{-2}$

a. Distances  $r$  and root mean-square amplitudes of vibration  $l$  in Å.  $k_s$  is the scale factor and  $\sum wA^2$  the weighted square error sum. Numbers in round brackets are uncorrected values for the standard deviations. Parameters in square brackets were not varied in the least squares iterations.

b, c, f. Results based upon the same intensities with  $w = \exp(-0.1(4-s)^2)$  for  $s < 4$ ,  $w = 1$  for  $4 \leq s \leq 15$ , and  $w = \exp(-0.006(s-15)^2)$  for  $s > 15$ . The scattering factor for bromine was based upon a relativistic potential.

b.  $r_{C_1-C_2}$ ,  $r_{C_1-Br_1}$ , and  $r_{Br_1 \cdots Br_4}$  are determined from a planar model ( $D_{2h}$ -symmetry) with the other distances as dependent variables.

c. Same as b, except that estimated values for a possible shrinkage effect (d) were included in the model.

d. Estimated values for a possible shrinkage effect for c.

e. Values for the root mean-square amplitudes of vibration calculated from spectroscopic data.<sup>6</sup>

f. The distance parameters are varied independent of any model.

g. Same as for iteration f, except that the scattering factor for Br was based upon a nonrelativistic potential.

h. Results from the data for the 48 cm plates only for  $s = 1.75$ , to  $s = 19.00$  in intervals of  $\Delta s = 0.25 \text{ \AA}^{-1}$ , and  $w = \exp(-0.1(s-4)^2)$  for  $s < 4.00$ ,  $w = 1$  for  $4 \leq s \leq 18$ , and  $w = \exp(-0.1(18-s)^2)$  for  $s > 18$ . The distances are varied independently.

i. Results from the data for the 19 cm plates only for  $\Delta s = 0.25$  and  $s_{\min} = 7$  and  $s_{\max} = 34 \text{ \AA}^{-1}$ , and  $w = \exp(-0.1(10-s)^2)$  for  $s < 10$ ,  $w = 1$  for  $10 \leq s \leq 30$ , and  $w = \exp(-0.1(s-30)^2)$  for  $s > 30$ . The distances are varied independently. The  $l$ -values were not varied and were the same as of h.

Table 2. Least squares results for the structure parameters of hexabromobenzene based upon four single and the average intensity curves

a	b	c	d	e	f	g	h
$r_{C_1-C_6}$	1.4101(0.0047)	1.3945(0.0041)	1.4034(0.0042)	1.4036(0.0043)	1.4033(0.0033)	1.4033	1.4033
$r_{C_1-Br_1}$	1.8840(0.0029)	1.8756(0.0026)	1.8898(0.0028)	1.8732(0.0027)	1.8803(0.0021)	1.8803	1.8803
$r_{C_1...Br_1}$	2.8559(0.0026)	2.8537(0.0026)	2.8510(0.0025)	2.8595(0.0026)	2.8550(0.0019)	2.8476	2.8537
$r_{C_1...Br_2}$	4.1633(0.0037)	4.1601(0.0034)	4.1560(0.0039)	4.1604(0.0044)	4.1613(0.0019)	4.1540	4.1664
$r_{C_1...Br_3}$	4.6860(0.0078)	4.6632(0.0093)	4.6670(0.0088)	4.6668(0.0095)	4.6714(0.0068)	4.6722	4.6869
$r_{Br_1...Br_2}$	3.3230(0.0023)	3.3151(0.0022)	3.3141(0.0020)	3.3074(0.0024)	3.3149(0.0017)	3.3149	3.2836
$r_{Br_1...Br_3}$	5.6933(0.0036)	5.6921(0.0034)	5.6873(0.0031)	5.6829(0.0034)	5.6894(0.0026)	5.6449	5.6875
$r_{Br_1...Br_4}$	6.5933(0.0059)	6.5523(0.0055)	6.5547(0.0053)	6.5493(0.0060)	6.5539(0.0043)	6.5462	6.5672
$l_{C_1-C_3}$	0.0675(0.0083)	0.0448(0.0079)	0.0504(0.0078)	0.0362(0.0093)	0.0492(0.0061)		
$l_{C_1-Br_1}$	0.0455(0.0056)	0.0086(0.0070)	0.0442(0.0055)	0.0206(0.0107)	0.0326(0.0053)		
$l_{C_1...Br_2}$	0.0592(0.0040)	0.0451(0.0044)	0.0572(0.0039)	0.0540(0.0044)	0.0543(0.0032)		
$l_{C_1...Br_3}$	0.0632(0.0054)	0.0561(0.0054)	0.0706(0.0052)	0.0747(0.0057)	0.0662(0.0041)		
$l_{C_1...Br_4}$	0.0566(0.0118)	0.0791(0.0113)	0.0725(0.0112)	0.0713(0.0122)	0.0707(0.0088)		
$l_{Br_1...Br_2}$	0.1266(0.0021)	0.1257(0.0020)	0.1177(0.0019)	0.1239(0.0022)	0.1235(0.0016)		
$l_{Br_1...Br_3}$	0.1204(0.0031)	0.1177(0.0030)	0.1112(0.0027)	0.1114(0.0030)	0.1152(0.0023)		
$l_{Br_1...Br_4}$	0.0961(0.0050)	0.0927(0.0047)	0.0912(0.0046)	0.0927(0.0051)	0.0933(0.0037)		
$k_S$	121.84(2.00)	123.02(1.91)	119.70(1.86)	118.44(1.96)	120.71(1.48)		
$\sum w\Delta^2 \times 10^{-6}$	1.50	0.76	0.66	0.83	0.45		(9.28°)

a. Distances  $r$  and root mean-square amplitudes of vibration  $l$  in Å units.  $k_S$  is the scale factor and  $\sum w\Delta^2$  is the weighted square error sum.

b-f. Numbers in parenthesis are uncorrected standard deviations.  $r_{C_1...C_6}$  and  $r_{C_1...C_4}$  were dependent variables based upon the geometry of a planar benzene ring, and the corresponding  $l$ -values were fixed at 0.055 and 0.050 Å, respectively, and not varied. The weighting function was for  $s < 4$ ,  $w = \exp(-0.1(4-s)^2)$ ,  $4 \leq s \leq 10$ ,  $w = 1$ , and for  $s > 10$ ,  $w = \exp(-(0.006(s-10))^2)$ . The curves were approximately on the same scale.

b-e. Results from four single intensity curves, each based upon the data from one plate from each of the three camera distances.

f. Results for the average of the four curves used for b-e.

g. Distances in a nonplanar model ( $D_{3d}$  symmetry) of the molecule with the  $C_1-C_2$ ,  $C_1-Br_1$ , and the  $Br_1...Br_2$  distance from f. The angle between the  $C_1-Br_1$  distance and the plane of the benzene ring is given.

h. Distances in a planar model ( $D_{6h}$  symmetry) of the molecule with the  $C_1-C_2$ , and the  $C_1-Br_1$  distance from f.



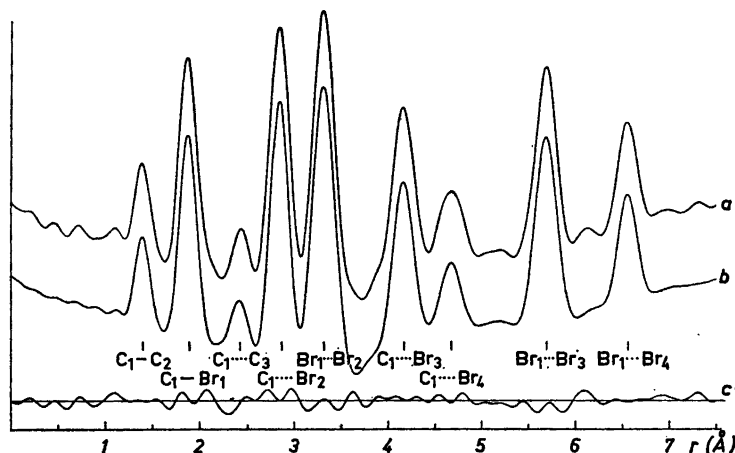


Fig. 6. Radial distribution functions for hexabromobenzene according to eqn. 5. A damping function of  $\exp(-0.0009 s^2)$  was applied. a: From the experimental molecular intensities. b: From the theoretical molecular intensities with parameters of Table 2, f, c: Difference.

#### DISCUSSION

*Tetrabromoethylene.* The distances in tetrabromoethylene determined with the distances as independent variables are in good agreement with values obtained for a model with  $D_{2h}$  symmetry, and the two iterations end at about the same weighted square error sum. If an estimated shrinkage effect is included in the model, the square error sum increases somewhat (Table 1, f, b, and c).

The experimental root mean-square amplitudes for the C—Br distances are smaller, and the Br—Br amplitudes are larger than the spectroscopic ones for both of the two different bromine scattering factors. The agreement with the calculated amplitudes for the C—Br distances are better for the scattering factor from the relativistic bromine potential (Table 1, f, g, and e). The final values for the most important distances and standard deviations including an estimate of systematic errors and errors due to possible correlation of the data<sup>17</sup> are given in Table 4.

The value obtained for the C=C bond of 1.362 Å is about 0.025 Å longer than the electron diffraction value for ethylene.<sup>18</sup> The difference seems to be significant, and the value for tetrabromoethylene is in good agreement with the electron diffraction value of 1.360 Å previously determined in *cis*-dibromoethylene.<sup>19</sup>

*Hexabromobenzene.* For hexabromobenzene it seems reasonable to assume one of the two following equilibrium configurations, either a planar undistorted configuration with  $D_{6h}$  symmetry, or a distorted configuration possessing  $D_{3d}$  symmetry with every second bromine atom above or below the plane of the benzene ring. For the latter configuration, a smaller distortion of the benzene

Table 3. Least squares results for the structure parameters of hexabromobenzene based upon the average intensities.

a	b	c	d	e	f	g
$r_{C-C_2}$	1.3985(0.0055)	1.3979(0.0046)	1.4028(0.0039)	1.3936(0.0053)	1.4021(0.0029)	1.4061(0.0020)
$r_{C-Br_1}$	1.8794(0.0025)	1.8801(0.0021)	1.8794(0.0018)	1.8847(0.0021)	1.8866(0.0030)	1.8863(0.0021)
$r_{C_1 \cdots Br_2}$	2.8552(0.0022)	2.8550(0.0019)	2.8574(0.0019)	2.8496(0.0018)	2.8584	2.8578
$r_{C_1 \cdots Br_3}$	4.1638(0.0036)	4.1613(0.0030)	4.1605(0.0028)	4.1615(0.0027)	4.1705	4.1695
$r_{C_1 \cdots Br_4}$	4.6691(0.0084)	4.6715(0.0070)	4.6768(0.0071)	4.6684(0.0058)	4.6908	4.6997
$r_{Br_1 \cdots Br_2}$	3.3142(0.0021)	3.3147(0.0018)	3.3163(0.0017)	3.3126(0.0017)	3.2887	3.3110(0.0021)
$r_{Br_1 \cdots Br_3}$	5.6890(0.0031)	5.6894(0.0026)	5.6884(0.0024)	5.6891(0.0023)	5.6963	5.6774
$r_{Br_1 \cdots Br_4}$	6.5550(0.0053)	6.5538(0.0044)	6.5543(0.0038)	6.5594(0.0043)	6.5775	6.5723
$l_{C-C_2}$	0.0442(0.0080)	0.0495(0.0062)	0.0472(0.0056)	0.0631(0.0103)	0.0466(0.0117)	0.0483(0.0078)
$l_{C-Br}$	0.0077(0.0270)	0.0328(0.0054)	0.0325(0.0052)	0.0262(0.0098)	0.0283(0.0111)	0.0326(0.0067)
$l_{C_1 \cdots Br_2}$	0.0416(0.0048)	0.0529(0.0032)	0.0565(0.0030)	0.0472(0.0046)	0.0438(0.0064)	0.0532(0.0040)
$l_{C_1 \cdots Br_3}$	0.0569(0.0057)	0.0663(0.0042)	0.0655(0.0038)	0.0688(0.0053)	0.0641(0.0078)	0.0660(0.0052)
$l_{C_1 \cdots Br_4}$	0.0629(0.0119)	0.0710(0.0090)	0.0741(0.0076)	0.0596(0.0113)	0.0697(0.0167)	0.0704(0.0112)
$l_{Br_1 \cdots Br_2}$	0.1227(0.0019)	0.1237(0.0016)	0.1205(0.0017)	0.1301(0.0018)	0.1258(0.0029)	0.1231(0.0021)
$l_{Br_1 \cdots Br_3}$	0.1134(0.0028)	0.1153(0.0023)	0.1132(0.0021)	0.1230(0.0024)	0.1134(0.0042)	0.1159(0.0029)
$l_{Br_1 \cdots Br_4}$	0.0917(0.0046)	0.0934(0.0038)	0.0931(0.0031)	0.1015(0.0048)	0.0947(0.0072)	0.0952(0.0049)
$k_S$	114.46(1.69)	120.90(1.51)	119.66(2.74)	123.17(1.30)	117.26(2.53)	120.01(1.82)
$\sum w\Delta^2 \times 10^{-6}$	0.67	0.47	0.33	0.24	1.61	0.75

a. Distances  $r$  and root mean-square amplitudes of vibration  $l$  in Å units.  $k$  is the scale factor and  $\sum w\Delta^2$  is the weighted square error sum.

b. Result of least squares iteration using scattering factors based upon a nonrelativistic potential for bromine.<sup>13</sup>  $r_{C_1 \cdots C_2}$  and  $r_{C_1 \cdots C_4}$  were set equal to 2.417 and 2.791 Å and the corresponding  $l$ -values were set equal 0.55 and 0.50 Å and not varied. The weighting function was for  $s < 4$ ,  $w = \exp(-0.1(4-s)^2)$ , for  $4 \leq s \leq 10$ ,  $w = 1$ , and for  $s > 10$ ,  $w = \exp(-0.006(s-10)^2)$ .

c. Result of iteration using scattering factors based on a relativistic potential for bromine.<sup>14-16</sup> Otherwise the same conditions as for b.

d. Same as for c, except that the weighting function was for  $s < 10$ ,  $w = \exp(-0.1(10-s)^2)$ ,  $10 \leq s \leq 20$ ,  $w = 1$ , and  $s > 20$ ,  $w = \exp(-0.1(s-20)^2)$ .

e. Same as for c, except the weighting function was for  $s \leq 10$ ,  $w = 1$ , and for  $s > 10$ ,  $w = \exp(-0.1(s-10)^2)$ .

f. The same conditions as for iteration c, except that  $r_{C_1-C_2}$  and  $r_{C_1-Br_1}$  are determined from a planar model ( $D_{6h}$ -symmetry) with the other distances dependent on these two distances and the geometry of the model.

g. The same conditions as for iteration c, except that  $r_{C_1-C_2}$ ,  $r_{C_1-Br_1}$ , and  $r_{Br_1 \cdots Br_2}$  are determined from a nonplanar model with a planar benzene ring and every second bromine atom above and below the plane of the benzene ring ( $D_{3d}$ -symmetry) with the other distances dependent on the former three distances and the geometry of the model. The results for the distances correspond to an angle of  $7.11(0.69)^\circ$  between  $r_{C_1-Br_1}$  and the plane of the benzene ring.

Table 4. Final results for the most important distances and estimated standard deviations for tetrabromoethylene and hexabromobenzene.

	$r_{\text{C-C}}$	$r_{\text{C-Br}}$	$r_{\text{Br}\cdots\text{Br}}$	$\varphi$
$\text{C}_2\text{Br}_4^a$	1.362 (0.009)	1.881 (0.003)	3.176 (0.004)	115.1 (0.3)
$\text{C}_6\text{Br}_6^b$	1.403 (0.005)	1.880 (0.004)	3.315 (0.004)	9.3 (1.1)
$\text{C}_6\text{Br}_6^c$	1.406 (0.004)	1.886 (0.004)	3.311 (0.005)	7.1 (1.5)

<sup>a</sup> Tetrabromoethylene. The molecule possesses  $D_{2h}$ -symmetry, and the  $\angle\text{BrCBr}$  is given.

<sup>b</sup> Hexabromobenzene. Results for the distances determined independent of a model. The angle between the C—Br bond and the plane of the benzene ring for a model possessing  $D_{3d}$  symmetry with every second bromine atom above or below this plane is given.

<sup>c</sup> Hexabromobenzene. Results for the distances with the model in b as geometric restrain in the least squares iteration.

ring might also take place, but this distortion is not included in the nonplanar model used for this molecule.

In Table 2 f, g, and h the  $\text{C}_1\text{—C}_2$ ,  $\text{C}_1\text{—Br}_1$  and, for the nonplanar case, the  $\text{Br}_1\cdots\text{Br}_2$  distance obtained from the least squares iteration with only a planar benzene ring as geometric restrain, have been used to calculate the other distances in the two models. Except for the  $\text{Br}_1\cdots\text{Br}_2$  distance, the other independently determined distances are in good agreement with the distances of the planar model, and most of the differences have the sign of a shrinkage effect. However, the experimental  $\text{Br}_1\cdots\text{Br}_2$  distance is about 0.03 Å longer than the corresponding value of the planar model. For the nonplanar model, the  $\text{Br}_1\cdots\text{Br}_3$  distance is about 0.04 Å shorter than the experimental one.

In Table 3 c, f, and g the results of least squares iterations with the two models as geometric restrain are given. The weighted square error sum for the nonplanar model is about half of the sum for the planar one, so the nonplanar configuration seems to fit the data better than the planar one. However, this sum is further reduced by one third for the iteration independent of a model. For hexabromobenzene, eight distances contribute significantly to the molecular intensities and the nonplanar model is described by only three distance parameters, so increased square error sums for the models might be expected. Studying the results from the four single intensity curves of Table 2 and the results for the two different weighting functions in Table 3 d and e, one cannot say that the results for the nonplanar model deviate significantly from the different independent results.

However, the results for tetrabromoethylene indicate that a really successful investigation of hexabromobenzene might have given better agreement between the independently determined distances and the distances of the correct model. It seems difficult to think of any other reasonable models for hexabromobenzene than the two previously mentioned, and including a shrinkage effect in the models or a distorted benzene ring in the nonplanar one will not

improve the agreement. For both of the proposed models one might imagine that the average Br...Br repulsive energy could be reduced somehow through the molecular vibrations leading to an observed Br<sub>1</sub>...Br<sub>2</sub> distance somewhat longer than the actual equilibrium distance. To make hexabromobenzene planar, this "negative shrinkage" effect would have to be about 0.03 Å which seems rather unlikely.

The experimental root mean-square amplitudes for the C—Br distances seem smaller than expected, and the best results are obtained for the bromine scattering factor for the relativistic potential. For the latter scattering factor, the weighted square error sum is reduced by about one third.

Comparing the results from this investigation with the results from the previous one,<sup>5</sup> the distances agree very well, but larger C—Br *l*-values were found in the earlier investigation. The two investigations are based upon partly different data, different backgrounds, weighting functions, modification functions and scattering factors so the results are not comparable. For the present investigation, the uncorrected standard deviations of the parameters have been reduced by about one third. An attempt to determine asymmetry constants for the shorter distances gave standard deviations larger than the least squares values of the constants.

*Theory.* For both of the molecules, the experimental C—Br amplitudes are smaller than expected. While this might be due to systematic experimental errors, it is more likely due to inaccuracies in the applied theory. The theory, as described earlier in the paper, involves several approximations. A nonrelativistic description should be adequate for the scattering from bromine and lighter atoms for 35 keV electrons in the *s*-range of the experimental data,<sup>20</sup> so the accuracy of the atomic scattering factors are limited by the accuracy of the atomic potential. Exchange effects are known to be small,<sup>21</sup> and a two parameters description of polarization indicates that this effect might be significant for heavier atoms at smaller *s*-values; however, the exact size of the effect is uncertain.<sup>22</sup> Bonding effects are supposedly small for the two molecules and would at least partly be included in the background.<sup>23</sup> Correction terms to the kinematic theory for molecular scattering have been given.<sup>24-26</sup> For molecules containing at least three heavy atoms, terms involving triple scattering might contribute intensities with fluctuations comparable to the periodicity of the molecular intensities. The intensities from these terms were calculated according to the expressions of Ref. 24 for both of the molecules, but the size of these terms was small in relation to the errors of the experimental data. Then the main uncertainties in the theory for the two molecules seem to be the accuracy of the atomic potential and the size and form of a possible polarization correction.

In this paper and the previous one,<sup>5</sup> the structure of hexabromobenzene has been investigated using a scattering factor for bromine according to the first Born approximation from a nonrelativistic HF potential, a partial waves scattering factor from the same potential, and partial waves scattering factor from a relativistic HFS potential, and steadily improved agreements with the experimental data were obtained. But the results of this investigation seem to indicate that the theory for the scattering from molecules of this type could still be improved upon in relation to the present experimental

accuracy. As expected, the experimental distances are not very much dependent on the applied theory for molecules where the different peaks on the radial distribution functions are reasonably well resolved. However, for molecules with closely spaced distances, for separating the torsional and the skeletal motions in certain types of molecules, for studying the distribution of internal rotational isomers, or for an accurate determination of the  $l$ -values, it might be important to use the best available theory.

*Acknowledgements.* The author wishes to thank *The Norwegian Research Council for Science and the Humanities* for financial support of this work. Thanks are also due to Dr. Jerry A. Peacher for use of the scattering factor computer program, to Dr. D. Liberman and Dr. H. L. Cox, Jr. for receiving the relativistic HFS calculations for bromine and the analytical fit of the radial density, respectively, prior to publication, to cand.real. Arne Almenningen for taking the electron diffraction pictures, and to the members of the Oslo electron diffraction group for helpful discussions.

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Received January 17, 1967.