

## The Molecular Structure of Hexafluorobenzene

### The Application of Least-Squares Calculation on the Electron Diffraction Intensity Data

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The structure of gaseous hexafluorobenzene has been studied by electron diffraction. The structure problem is well suited for a least-squares refinement based on intensity data. A series of least-squares calculations using various assumptions has been performed. The method is found useful, though it was impossible to obtain really realistic error limits in spite of a rather thorough analysis of the possible error sources.

The equilibrium conformation of hexafluorobenzene does not seem to deviate significantly from the planar form, though there is evidence for a certain shrinkage. The values obtained for the bond distances are  $r_{C-C} = 1.394 \pm 0.007 \text{ \AA}$  and  $r_{C-F} = 1.327 \pm 0.007 \text{ \AA}$ .

#### EXPERIMENTAL

The sample of hexafluorobenzene was obtained from Dr. D. R. MacKenzie, Brookhaven National Laboratory. Diffraction photographs were taken in the usual way at a nozzle temperature of about 14°C. Three camera distances were used (48.145, 19.433, and 12.199 cm), and intensity data were thus obtained from  $s = 1.50 \text{ \AA}^{-1}$  to  $s = 60.00 \text{ \AA}^{-1}$ .

At each distance four plates were selected and treated according to the usual procedure at this institute.<sup>1</sup>

#### STRUCTURE ANALYSIS

The molecular intensity may be expressed as

$$I(s) = \text{const} \sum \frac{A_i(s)}{r_i} \exp\left(-\frac{1}{2} u_i^2 s^2\right) \sin r_i s \quad (1)$$

$r$ : interatomic distance

$u$ : root mean-square amplitude of vibration.

The sum is taken over all different interatomic distances. If the same distance between two atoms,  $k$  and  $l$ , occurs  $n_{kl}$  times,  $A_i(s)$  may be expressed as follows:

$$A_i(s) = n_{kl} Z_k Z_l \frac{[1 - (F/Z)]_k [1 - (F/Z)]_l}{[1 - (F/Z)]_m [1 - (F/Z)]_{ni}} \quad (2)$$

In our case a reasonable choice is  $m = C$  and  $n = F$ .  $A$  is then a constant for the CF distances, but will vary slightly with  $s$  for the CC and FF distances. In most of this work, however,  $A$  is assumed to be a constant for all the distances. This approximation has been applied if nothing else is stated.  $F$ -values were taken from Berghuis *et al.*<sup>2</sup> and Freeman<sup>3</sup> for C and F, respectively.

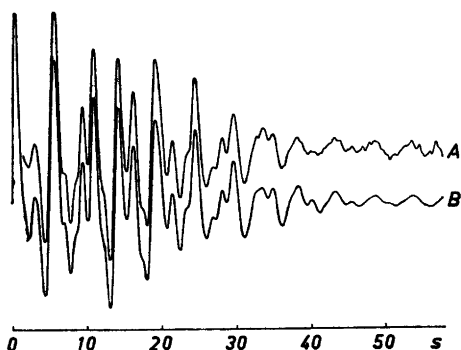


Fig. 1. Experimental (A) and theoretical (B) intensity curves. The theoretical curve was calculated using the data in Table 1.

The experimental molecular intensity is shown in Fig. 1, where it can be compared with a theoretical intensity curve calculated using the final parameters from Table 1. A series of experimental radial distribution (RD) functions was calculated from

$$\sigma(r)/r = \int \exp(-ks^2) I_{\text{obs}} \sin rs \, ds \quad (3)$$

where  $k$  is an artificial damping factor. The RD curve with  $k = 0.0009$  is shown in Fig. 2. The three inner peaks are all composed of contributions from two different interatomic distances. Assuming a planar hexagonal molecule, it was easy to make rather good estimates for the two independent distances

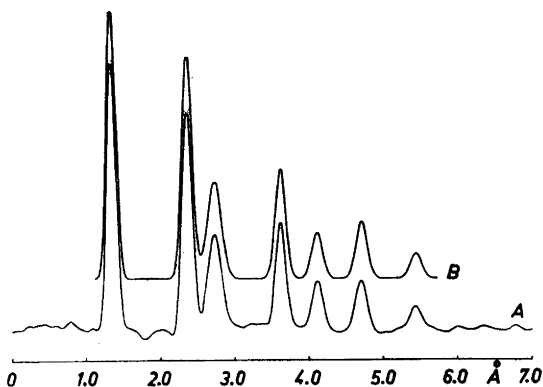


Fig. 2. Experimental (A) and theoretical (B) RD curves.  $k = 0.0009$ . The theoretical curve was calculated using the data in Table 1.

Table 1. Structure of  $C_6F_6$ . Distances ( $r$ ) and root-mean-squares amplitudes of vibration ( $u$ ) in Å.

		$r$	$u$
1	$C_1-F_1$	1.327	0.031
2	$C_1-C_2$	1.394	0.030
3	$C_1-C_3$	2.414	0.046
4	$C_1-C_4$	2.788	0.057
5	$F_1-F_2$	2.721	0.085
6	$F_1-F_3$	4.713	0.067
7	$F_1-F_4$	5.442	0.063
8	$C_1-F_2$	2.357	0.050
9	$C_1-F_3$	3.625	0.055
10	$C_1-F_4$	4.115	0.060

(i.e. the C—C and C—F bond distances). Fig. 2 shows also a theoretical RD curve calculated using the results in Table 1. The fit is satisfactory, but the maxima of the two outer peaks of the theoretical curve are shifted a few thousands of an Å to the right, while the inner peak is shifted 0.0008 Å to the left compared to the experimental curve. It is reasonable to ascribe these differences to shrinkage. If 0.0008 Å is added to the two bond distances, and the dependent distances are calculated from the adjusted values, the results in Table 2 *a* are obtained. The maximum positions of the four peaks of the experimental RD curve containing only one distance, are presented in Table 2 *b*. The differences between the values in Table 2 *a* and *b* give the shrinkage effect and are shown in Table 2 *c*. These differences may be compared with the shrinkage effect calculated from spectroscopic data by Cyvin *et al.*<sup>4</sup>

Table 2. The shrinkage effect in hexafluorobenzene. All values in Å.

	<i>a</i>	<i>b</i>	<i>c</i>	<i>d</i>	<i>e</i>
1	1.327 <sub>g</sub>	—	—	—	—
2	1.394 <sub>g</sub>	—	—	—	—
3	2.415 <sub>g</sub>	—	—	0.0033	0.0019
4	2.789 <sub>g</sub>	—	—	0.0046	0.0028
5	2.722 <sub>g</sub>	—	—	0.0058	0.0069
6	4.715 <sub>g</sub>	4.707 <sub>g</sub>	0.008 <sub>g</sub>	0.0145	0.0107
7	5.445 <sub>g</sub>	5.435 <sub>g</sub>	0.009 <sub>g</sub>	0.0181	0.0130
8	2.358 <sub>1</sub>	—	—	0.0042	0.0033
9	3.627 <sub>1</sub>	3.620 <sub>g</sub>	0.006 <sub>g</sub>	0.0090	0.0062
10	4.117 <sub>g</sub>	4.120 <sub>g</sub>	—0.002 <sub>g</sub>	0.0110	0.0075

*a* Distances ( $r_m$ ) corresponding to a planar model without shrinkage.

*b* Positions of the maximum of the peaks in the experimental RD curve.

*c* Difference between *a* and *b*.

*d* Shrinkage corresponding to  $r_g$  distances.<sup>4</sup>

*e* Shrinkage corresponding to  $r_m$  distances.

The shrinkages given in Ref.<sup>4</sup> are shown in Table 2 *d*. These values refer to  $r_g$ -distances, corresponding to the center of gravity of the probability function  $\sigma(r)$ . If the peak in the  $\sigma(r)$  curve is symmetrical, the relation between  $r_g$  and the position of maximum of the peak ( $r_m$ ) in the  $\sigma(r)/r$  curve may be expressed as

$$r_g \approx r_m + u^2/r_m \quad (4)$$

The shrinkage referring to  $r_m$ -values has been calculated by means of eqn. 4 and  $u$ -values from Cyvin *et al.*<sup>4</sup> The results are given in Table 2 *e*. The agreement between the results in Table 2 *c* and *e* is satisfactory except for distance 10 where our value is negative.

The model was then refined by the least-squares method.<sup>5-7\*</sup> The refinement was performed on an IBM 1620 computer. The final results given in Table 1 are based on the least-squares results.

#### DISCUSSION OF THE LEAST-SQUARES REFINEMENT OF THE INTENSITY CURVE

The least-squares programme makes it possible to perform refinements both with  $A$  constant and as a function of  $s$  (see eqn. 1). The weighting scheme used was of the form

$$\begin{aligned} W &= \exp [-W_1 (s_1 - s)] \text{ for } s < s_1 \\ W &= 1.00 \quad \quad \quad \gg s_1 \leq s \leq s_2 \\ W &= \exp [-W_2 (s - s_2)] \quad \gg s > s_2 \end{aligned}$$

$s_1$ ,  $s_2$ ,  $W_1$ , and  $W_2$  are constants to be chosen by the user of the programme.

Table 3 shows results from various least-squares refinements. The special conditions are given in each case. The standard deviations are those directly obtained from the least-squares calculations without corrections.

The quantity  $\Sigma W \Delta^2$  included in the table is the sum

$$\sum_{s_{\min}}^{s_{\max}} \text{Weight} \times (I_{\text{obs}} - I_{\text{calc}})^2$$

It is a measure of the over all fit, but since background defects contribute considerably to this quantity, the criterium of small  $\Sigma W \Delta^2$  values should be used critically. A comparison of  $\Sigma W \Delta^2$  values is of course, only possible when the  $s$ -range and the weighting scheme are the same.

The agreement between the results in Table 3 *a*, *b*, *c*, *d*, and *e* is satisfactory. The only difference between the refinements *a* and *b* is in the weighting scheme constants. The difference between the parameter results is smaller than any optimistic error estimate would suggest in spite of the substantial differences in weighting-scheme constants. The standard deviations are slightly different in the two cases. Using  $A_{\text{CC}}$  and  $A_{\text{FF}}$  as functions of  $s$  (Table 3 *c*) nearly identical results are obtained as with  $A$  constant for all the distances. Contrary to

\* The least-squares programme was written in Fortran II by one of the present authors (H.M.S.).

what may be expected  $\Sigma W\Delta^2$  is greater in *c* than in *a*, though the difference is small. However, the theoretical intensity curves corresponding to *a* and *c* differ only at low *s*-values. (When  $s > 10$  the two curves are almost identical). The fitting of the background is usually subject to uncertainties at low *s*-values. The background was in this case adjusted by comparing the experimental curve to the theoretical curve based on the data in Table 3 *a*. If the data in *c* had been used for background adjustment  $\Sigma W\Delta^2$  of *c* would certainly have been reduced.

A planar model with the shrinkage for the longer distances calculated by Cyvin *et al.*<sup>4</sup> (Table 2 *b*) was also refined (*d*). The interatomic distances were calculated from the bond lengths as above and then corrected for the shrinkage effect by subtracting the shifts given in Table 2 *e*. No great changes are observed, although, as should be expected, the C—C bond distance is slightly longer.  $\Sigma W\Delta^2$  is a trifle larger than in *a*, but the standard deviations for the *r*-values are slightly reduced.

Table 3. Least-squares results. Standard deviations are given in brackets.  $\Delta s = 0.25 \text{ \AA}^{-1}$  in all cases. *r* and *u* in  $\text{\AA}$ .

	<i>a</i>	<i>b</i>	<i>c</i>	<i>d</i>	<i>e</i>
$r_1$	1.327 <sub>1</sub> (0.0008)	1.327 <sub>6</sub> (0.0006)	1.327 <sub>0</sub> (0.0008)	1.327 <sub>8</sub> (0.0007)	1.327 <sub>5</sub> (0.0008)
$r_2$	1.393 <sub>9</sub> (0.0007)	1.393 <sub>4</sub> (0.0006)	1.394 <sub>1</sub> (0.0007)	1.396 <sub>7</sub> (0.0006)	1.395 <sub>0</sub> (0.0007)
$r_5$					2.727 <sub>2</sub> (0.0021)
$u_1$	0.031 (0.0013)	0.032 (0.0010)	0.029 (0.0014)	0.029 (0.0012)	0.030 (0.0012)
$u_2$	0.029 (0.0022)	0.032 (0.0016)	0.028 (0.0023)	0.029 (0.0021)	0.029 (0.0021)
$u_3$	0.045 (0.0026)	0.047 (0.0023)	0.044 (0.0027)	0.042 (0.0024)	0.045 (0.0025)
$u_4$	0.057 (0.0065)	0.058 (0.0066)	0.055 (0.0068)	0.052 (0.0058)	0.071 (0.0100)
$u_5$	0.085 (0.0022)	0.086 (0.0026)	0.084 (0.0023)	0.085 (0.0021)	0.083 (0.0023)
$u_6$	0.067 (0.0027)	0.068 (0.0030)	0.066 (0.0029)	0.067 (0.0026)	0.067 (0.0026)
$u_7$	0.063 (0.0058)	0.062 (0.0062)	0.062 (0.0062)	0.063 (0.0058)	0.063 (0.0056)
$u_8$	0.050 (0.0009)	0.051 (0.0008)	0.049 (0.0009)	0.049 (0.0009)	0.049 (0.0009)
$u_9$	0.055 (0.0013)	0.056 (0.0013)	0.054 (0.0014)	0.055 (0.0013)	0.055 (0.0013)
$u_{10}$	0.060 (0.0031)	0.060 (0.0033)	0.059 (0.0034)	0.060 (0.0031)	0.060 (0.0030)
Scale	0.900 (0.0067)	0.906 (0.0082)	0.883 (0.0070)	0.901 (0.0067)	0.900 (0.0066)
$\Sigma = W\Delta^2$	$3.74 \times 10^4$	$7.25 \times 10^4$	$4.37 \times 10^4$	$3.77 \times 10^4$	$3.58 \times 10^4$
$s_{\min}$	3.00	3.00	3.00	3.00	3.00
$s_{\max}$	58.00	58.00	58.00	58.00	58.00
$s_1$	7.00	5.00	7.00	7.00	7.00
$s_2$	15.00	50.00	15.00	15.00	15.00
$W_1$	0.15	0.15	0.15	0.15	0.15
$W_2$	0.06	0.06	0.06	0.06	0.06

*a, b* Planar model (2 independent distances).

*c* Planar model. *A* a function of *s* for CC and FF distances.

*d* Planar model with shrinkage (*cf.* Table 2 *e*).

*e* Non-planar model (3 independent distances).

Table 3, (continued).

	<i>f</i>	<i>g</i>	<i>h</i>	<i>i</i>	
$r_1$	1.326 (0.0017)	1.324 (0.0011)	1.320 (0.0014)	1.336 <sub>a</sub> (0.0012)	
$r_2$	1.395 (0.0013)	1.397 (0.0009)	1.398 (0.0012)	1.385 <sub>b</sub> (0.0009)	
$r_3$	—	—	—	—	
$u_1$	0.029 (0.0031)	0.018 (0.0041)	0.020 (0.0050)	0.043 —	
$u_2$	0.026 (0.0054)	0.008 (0.011)	0.010 (0.01)	0.046 —	
$u_3$	0.046 (0.0046)	0.033 (0.0041)	0.040 (0.0062)	0.053 —	
$u_4$	0.055 (0.0102)	0.058 (0.0111)	0.061 (0.0169)	0.057 —	
$u_5$	0.083 (0.0041)	0.081 (0.0036)	0.076 (0.0047)	0.105 —	
$u_6$	0.071 (0.0053)	0.065 (0.0045)	0.068 (0.0067)	0.074 —	
$u_7$	0.072 (0.0122)	0.052 (0.0084)	0.054 (0.0122)	0.062 —	
$u_8$	0.048 (0.0017)	0.045 (0.0017)	0.046 (0.0023)	0.062 —	
$u_9$	0.056 (0.0023)	0.048 (0.0021)	0.050 (0.0030)	0.061 —	
$u_{10}$	0.057 (0.0052)	0.059 (0.0054)	0.052 (0.0067)	0.060 —	
Scale	0.886 (0.0197)	2.15 (0.0042)	1.651 (0.047)	0.956 (0.0079)	
$\Sigma = W\Delta^2$	$1.14 \times 10^5$	$5.71 \times 10^5$	$6.65 \times 10^5$	$8.14 \times 10^4$	
$s_{\min}$	7.50	6.75	6.75	3.00	
$s_{\max}$	45.00	45.00	45.00	58.00	
$s_1$	11.00	10.00	10.00	7.00	
$s_2$	30.00	22.00	22.00	15.00	
$\bar{W}_1$	0.08	0.10	0.10	0.15	
$\bar{W}_2$	0.04	0.06	0.06	0.06	

*f* Planar model. Intensity values from one camera distance only (4 plates).

*g, h* Planar model. Intensity values from one plate only.

*i* Planar model. *u*-Values (from Cyvin *et al.*<sup>4</sup>) not refined.

A model with planar carbon skeleton, but with the fluorine atoms alternately above and below the plane was tried (*e*). The third independent distance parameter was then the  $F_1 \cdots F_2$  distance. We note that  $\Sigma W\Delta^2$  is smaller in *e* than in *a*.

The deviation from planarity in terms of the angle ( $\varphi$ ) between the C—F bond and the carbon plane calculated from the values in Table 3 *e* is  $4.9^\circ$ . The standard deviation of  $\varphi$  is  $0.8^\circ$  calculated from the equation<sup>7</sup>

$$M = S^2 G B^{-1} \tilde{G} \quad (5)$$

The standard deviation of  $\varphi$  is undoubtedly subject to uncertainty of the kind to be discussed later for the distance parameters. It should be noted that a particular difficulty arises when  $\varphi$  approaches zero. The first derivative of the longer distances with respect to  $r_3$  is zero, and the approximation on which the least-squares procedure is based, does not hold. If the starting model is close enough to the final model, the refinement procedure works successfully even for very small  $\varphi$  values, though the starting model must of course not be exactly planar. Further, eqn. 5 from which the standard deviation of  $\varphi$  was calculated, is not a very good approximation for small  $\varphi$  values. (*Cf.* Ref.<sup>7</sup>)

Table 4. The moment matrix (times  $10^8$ ).  $r$  and  $u$  in Å.

	$r_1$	$r_2$	$u_1$	$u_2$	$u_3$	$u_4$	$u_5$	$u_6$	$u_7$	$u_8$	$u_9$	$u_{10}$	Scale
$r_1$	71.6												
$r_2$	-43.7	50.3											
$u_1$	71.0	-58.3	167.9										
$u_2$	139.3	-97.1	231.2	473.1									
$u_3$	52.9	18.5	49.4	115.6	660.9								
$u_4$	36.1	36.1	35.4	89.0	188.8	4174.6							
$u_5$	22.7	-43.5	56.3	78.9	-67.2	-372.5	484.6						
$u_6$	4.9	-2.3	25.0	36.5	27.9	33.1	12.4	724.6					
$u_7$	4.0	-2.2	23.9	34.3	25.7	30.2	12.9	12.2	3379.2				
$u_8$	25.7	-26.6	52.0	81.4	10.2	18.3	20.1	16.7	16.2	87.6			
$u_9$	4.5	-2.5	23.2	33.6	24.5	26.1	11.7	15.8	15.1	15.3	179.6		
$u_{10}$	4.3	-0.9	23.9	34.9	29.1	33.1	11.9	24.5	15.5	15.6	15.5	989.4	
Scale	79.1	-40.1	413.4	599.1	449.0	520.7	210.0	271.9	265.6	273.3	248.8	269.9	4474.1

and p. 78 of the same book). The real error distribution should obviously be unsymmetrical; a smaller  $\varphi$  value being more probable than a larger one. It is reasonable to ascribe the apparent deviation from planarity to shrinkage rather than assuming a non-planar equilibrium conformation.

Table 2 *f*, *g*, and *h* show that slightly different results are obtained when the refinement is based only upon a limited fraction of the experimental data available. In cases where data from only one plate were used (*g* and *h*) the results are particularly uncertain for the parameters  $u_1$  and  $u_2$ .

$u$ -Values may be calculated from spectroscopic data. This has been done for hexafluorobenzene by Cyvin *et al.*<sup>4</sup> The agreement between the results from the two different methods is rather poor for strongly overlapping distances. These distances go in pairs and are the following:  $C_1-F_1$  and  $C_1-C_2$  (distance 1 and 2),  $C_1-C_3$  and  $C_1-F_2$  (distance 3 and 8), and  $C_1-C_4$  and  $F_1-F_2$  (distance 4 and 5). In spite of the small standard deviation found by the least-squares refinements the possibility of rather large errors in the  $u$ -values for overlapping distances must be admitted for reasons to be described below. According to experience, spectroscopically calculated  $u$ -values are quite reliable for this kind of molecule and are in this case probably better than the electron diffraction values. It ought to be noted that the  $u$ -values for the F...F distances are decreasing in the order  $F_1...F_2$ ,  $F_1...F_3$ ,  $F_1...F_4$ . This result is obtained by both methods, though the corresponding values are somewhat different. The results in Table 3 *i* are obtained using  $u$ -values from Cyvin *et al.*<sup>4</sup> and refining only the two bond distances and the scaling factor, keeping all the  $u$ -values constant. As expected an increase in the C-F distance and a decrease in the C-C distance are obtained. The standard deviations are of course, somewhat increased for both distances.  $\Sigma W\Delta^2$  is also considerably increased.

Table 4 gives the moment matrix (**M**) corresponding to the results in Table 3 *a*. The diagonal term  $M_{ii}$  is equal to the square of the standard deviation.

tion ( $\sigma_i$ ) of the parameter  $i$ . The correlation coefficients ( $\rho_{ij}$ ) may be calculated from  $M$  by the formula

$$\rho_{ij} = M_{ij}/\sigma_i\sigma_j \quad (6)$$

We note that  $\rho$  is large where great correlation is to be expected. Of special interest is the correlation between the parameters  $r_1$ ,  $r_2$ ,  $u_1$ , and  $u_2$ . All the six correlation coefficients involved for the mentioned four parameters are large and have the expected signs. If for example  $u_2$  is increased,  $u_1$  will also increase, while the difference between the C—F and C—C bond lengths are decreased.

For various reasons the standard deviations obtained from the least-squares analysis of electron diffraction intensity data are unreliable. As a matter of well understood experience they tend to be too small.<sup>6</sup> An uncertain factor in the least-squares procedure is the choice of weighting scheme. The weighting of the data does influence the standard deviations (as well as the parameters). However, different constants have been tried in the weighting scheme mentioned without causing appreciable changes. (Table 3 *a* and *b*). It is possible that a more sophisticated weighting scheme where the weight is not a function of  $s$  only, could introduce further changes,<sup>8</sup> but the main feature of the results would certainly be maintained. For the discussion of some other factors that influence the standard deviations it is necessary to consider the treatment of the photometer curves. In the usual procedure of this laboratory the photometer curves are transferred to tracing paper. At the same time small irregularities, for instance due to film granularity and noise in the amplifier, are more or less smoothed out. In this way the intensity curve used for least-squares refinement, will often have very small random errors while systematic errors are not reduced. The intensity curve may by this procedure easily be slightly too high or too low over a considerable  $s$ -range. In other words the correlation between neighbouring points on the intensity curve is increased. This will obviously influence the  $u$ -values more than the distance parameters. This smoothing procedure may influence the damping of the intensity curve, but to no great extent the periodicity. The distance parameters should accordingly be mainly influenced through their correlation to the  $u$ -values. Though the mentioned smoothing out may increase the accuracy of the parameter determination by removing coarse errors and also to a certain extent random errors, it definitely obscures the error estimation by reducing the standard deviations unrealistically.

In the case of  $C_6F_6$  the contribution to the intensity curve from the  $C_1-F_1$  and  $C_1-C_2$  distances will almost cancel in the region  $s \approx 35 \text{ \AA}^{-1}$  to  $s \approx 55 \text{ \AA}^{-1}$  if the  $u$ -values are not too different. This region is usually of great importance for the determination of  $u$ -values of the order of magnitude expected here. Small systematic errors in the intensity curve particularly in the said  $s$ -range, will easily cause considerable errors in  $u_1$  and  $u_2$ . As mentioned the correlation coefficient between these  $u$ -values is great and positive (0.82). Thus they will change in the same direction.

Other factors that mainly influence the  $u$ -values are errors in photographic blackness correction and the form factors. The blackness correction introduces



uncertainties in each photometer curve and in addition makes the scaling of photometer curves of different  $s$ -range uncertain.

In spite of a thorough analysis of the possible sources of errors we are unable to produce a really reliable estimate of the error limits. For the reasons given above  $u$ -values are more influenced by some systematic errors than are the distance parameters, though an error in the wave length or camera distance will of course influence the  $r$ -values. In evaluating the error limits for the bond distances it seems inevitable to include knowledge based upon accumulated experience in the field of electron diffraction. The fact that the two bond distances overlap is compensated by the fact that the molecule has few geometric parameters. In terms of the RD curve two (in the non-planar case three) parameters are determined from seven well resolved peaks. It seems at the present state of development not possible to get a real useful absolute error estimate from the least-squares calculation. The error limit for the bond distances is estimated to 0.007 Å, but it should be emphasized that this value is presented with all reservations. The error in the difference of the two bond distances is not symmetric, a smaller value being more probable than a larger. The  $u$ -values for distances that do not overlap are probably rather well determined; the accuracy depending heavily on the weight of the distance (*cf.* eqn. 1). This fact is also seen from the standard deviations.

Even if the estimation of the real errors from the standard deviations obtained by least-squares refinement is rather difficult, at least if the experimental data are treated as present, the method is an important tool in the analysis of electron diffraction data. Usually both Fourier transformation and least-squares refinement ought to be used and the problem at hand must determine to what extent each method should be utilized. If the structure is not too complex, accurate values are often found rather quickly from a rough trial method by least-squares refinement, and for more complex structures one may often refine some of the parameters by this method, though for particularly large molecules little experience of the use of least-squares calculation has so far been obtained.

#### DISCUSSION OF THE STRUCTURE

The C—C bond length in hexafluorobenzene is, within the error limits, the same as in benzene.<sup>9</sup> The same bond length is also found in hexachloro- and hexabromobenzene.<sup>10</sup> The equilibrium conformation does not seem to deviate significantly from the planar form, a result also obtained for benzene and hexachlorobenzene. For the fluoroethylenes there is a certain evidence for a small shortening of the C—C bond length with increasing number of fluorine atoms,<sup>11</sup> though for lack of accurate experimental data the effect is somewhat uncertain. The C—C bond length in *cis*-difluoroethylene is 1.324 Å<sup>11</sup> compared to 1.337 Å in ethylene.<sup>12</sup> We can not exclude a small shortening of the C—C bond in hexafluorobenzene compared to benzene, but the effect is certainly very small and should not exceed 0.01 Å. The C—F bond distance is somewhat shorter than that found in vinylfluoride (1.347 Å<sup>13</sup>) and in *cis*-difluoroethylene (1.337 Å<sup>11</sup>).

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