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An Electron Diffraction Investigation of the Molecular Structure of Hexachloroethane in the Vapour Phase

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The electron diffraction method was used to determine the structure of hexachloroethane in the vapour phase. The molecule was found to have the staggered configuration and the molecular parameters were determined to be the following: C—C 1.564 ± 0.014 Å (u = 0.037 ± 0.015 Å), C—Cl 1.769 ± 0.003 Å (u = 0.059 ± 0.005 Å) and ∠CCCl 110.0 ± 0.5°.

The carbon-carbon interatomic distance is of special interest in the field of organic structural chemistry. Many attempts have been made by theoreticians as well as by experimentalists to explain the influence on the C—C distance of various adjacent substituents, but the different theories often disagree seriously. The bond-length variations that one seeks to explain are often of the same order of magnitude as the error limits of the experimental data that are available. It is accordingly of great value to determine the structure of a number of simple organic molecules with high precision.

The influence of adjacent electronegative groups on the carbon-carbon single bond distance is one of the effects about which very little is known. High precision determinations of the carbon-carbon distance in halogen substituted ethanes will help to elucidate this effect.

The molecular structure of hexachloroethane has been studied previously by means of X-ray [1] and electron diffraction.[2–6] For the carbon-carbon distance the discrepancy between the highest and lowest published value is as great as 0.2 Å, and a reinvestigation of the molecule therefore seemed to be desirable. The latest structural investigations of hexachloroethane are those by Swick, Karle and Karle [5] and by Morino and Hirota.[6] The former authors gave the following parameters: C—C $1.57^{+0.10}_{-0.07}$ Å, C—Cl 1.74 ± 0.01 Å and ∠ CCCl $109°40'^{+45'}_{-1°30'}$.

Morino and Hirota have determined the molecular parameters from a correlation method and from radial distribution curves. Their results using the two methods were: C—C $1.49_9^{+0.05}_{-0.03}$ Å (1.46_3 Å), C—Cl 1.76_3 ± 0.02 Å

(1.77_5 Å) and ∠CCCl 110°43′ ± 1°30′ (111° 29′). The numbers in the brackets refer to the radial distribution method. They have also tried to determine the carbon-carbon distance from the different nonbonded distances in the molecule, and the results obtained varied from 1.42_0 Å to 1.46_9 Å.

THE PRESENT STUDY

Electron diffraction diagrams were taken at two different distances between the scattering point and the photographic plate (approximately 48 and 19 cm). A modified s^3 sector was employed. The 48 cm and 19 cm diagrams covered s ranges of 1.25—21.00 Å^{-1} and 8.00—47.00 Å^{-1}, respectively.

The photometer curves were transferred into intensity values; the usual corrections were carried out.[7] The theoretical background was fitted to the intensity curves according to the equation

$$B_e(s) = k_1 B_t(s) + k_2 \qquad (1)$$

where $B_t(s)$ and $B_e(s)$ are the theoretical background and the adjusted theoretical background, respectively, as presented from photometer curve. The constant k_1 defines the ordinate scale of the intensities and the constant k_2 takes account of extraneous scattering which is observed to be approximately constant over the entire photographic plate. This extraneous scattering is not yet fully understood, but an explanation is being sought. As will be understood by eqn. (1) the adjustment is performed before the various corrections are carried out.

Fig. 1 shows the 48 cm intensity curve with theoretical background fitted in. The correspondence is satisfactory, but minor corrections, especially in the

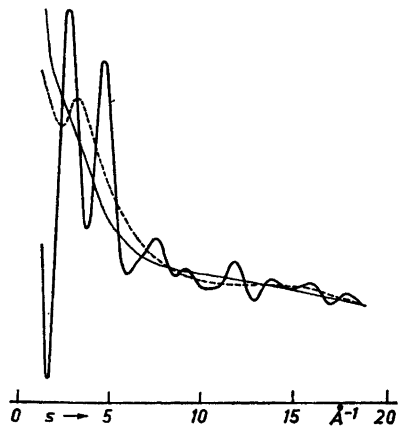

Fig. 1. Hexachloroethane. 48 cm intensity curve with theoretical (fully drawn) and experimental (plotted) background.

inner region ($s < 7$ Å^{-1}) had to be made. The experimental background plotted on the figure is the final background used in this investigation. The first backgrounds were refined in several ways as, for example, by comparison of experimental and theoretical intensity curves. The background scattering

was subtracted from the total scattered intensities and the overlap region of the 48 cm and 19 cm curves was averaged.

With the assumptions (1) that no phase shift occurs during the scattering process and (2) of harmonic vibrations of the atomic nuclei, the following equation can be given for the molecular part of the scattered intensity:

$$I_m(s)=\sum_{i\neq j}(Z_i-F_i)(Z_j-F_j)\exp(-u_{ij}^2\cdot s^2/2)\cdot\sin(sr_{ij}^e)/(sr_{ij}^e) \qquad (2)$$

Z_i: atomic number of atom i
F_i: X-ray atomic form factor of atom i
$s = (4\pi/\lambda)\sin\Theta$
2Θ: electron scattering angle
λ: electron wavelength
r_{ij}^e: equilibrium distance between atom i and atom j
u_{ij}: root-mean-square deviations from the equilibrium interatomic distances r_{ij}^e

If the molecular intensity function (2) is multiplied by a modification function

$$\varphi(s) = \frac{s\cdot\exp(-ks^2)}{[(Z_l-F_l)/Z_l][(Z_m-F_m)/Z_m]} \qquad (3)$$

where k is a constant and the approximation

$$\frac{[(Z_i-F_i)/Z_i][(Z_j-F_j)/Z_j]}{[(Z_l-F_l)/Z_l][(Z_m-F_m)/Z_m]} \approx 1 \qquad (4)$$

is used, the molecular intensity is corrected for non-nuclear scattering. The modified molecular intensity function is given by

$$I'_m(s)=\sum_{i\neq j}\frac{Z_iZ_j}{r_{ij}^e}\exp[-(u_{ij}^2+2k)s^2/2]\cdot\sin(sr_{ij}^e) \qquad (5)$$

A Fourier transform of the modified intensity function gives a modified radial distribution function represented by

$$\frac{\sigma'(r)}{r} = \frac{2}{\pi}\int_0^\infty I'_m(s)\cdot\sin(sr)\mathrm{d}s \approx \frac{1}{\sqrt{2\pi}}\sum_{i\neq j}\frac{Z_iZ_j}{r_{ij}^e\sqrt{u_{ij}^2+2k}}\exp\left[-\frac{(r_{ij}-r_{ij}^e)^2}{2u_{ij}^2+4k}\right] \qquad (6)$$

If l and m in eqn. (4) are chosen equal to i and j, the contributions to the radial distribution curve from distances between atoms of type i and type j are Gaussian peaks with weight factors equal to

$$(n_{ij}/r_{ij}^e)Z_iZ_j$$

where n_{ij} is the number of times the distance in question occurs.

The contributions from the other types of distances are not exactly Gaussian due to failure in approximation (4). If all the F-curves have nearly similar forms the deviations from the Gaussian shape are not very large, but should be taken into account.

When the maximum difference between the atomic numbers in a molecule does not exceed 10, approximation (4) may usually be used with good results for all kind of distances, if Z_i and Z_j in eqn. (6) are replaced by Z_i' and Z_j', and

Z_l and Z_m are chosen properly. The weight factors Z_i' and Z_j' are chosen so that the theoretical and experimental areas of the radial distribution curves are as alike as possible.

In hexachloroethane the difference in atomic numbers between the two kind of atoms is 11, and this is therefore a limiting case. There are three kind of distances, namely C—C, C—Cl and Cl—Cl distances. In this investigation three principally different modification functions of type (3) were used, namely

$$\varphi_1(s) = \frac{s \cdot \exp(-ks^2)}{[(Z_C - F_C)/Z_C]^2} \tag{7}$$

$$\varphi_2(s) = \frac{s \cdot \exp(-ks^2)}{[(Z_C - F_C)/Z_C][(Z_{Cl} - F_{Cl})/Z_{Cl}]} \tag{8}$$

$$\varphi_3(s) = \frac{s \cdot \exp(-ks^2)}{[(Z_{Cl} - F_{Cl})/Z_{Cl}]^2} \tag{9}$$

The radial distribution curves modified by the functions $\varphi_1(s)$, $\varphi_2(s)$, or $\varphi_3(s)$ will give the C—C, C—Cl or Cl—Cl distances, respectively, as Gaussian-shaped peaks, if harmonic vibrations of the nuclei are assumed. By studying, for all three cases, the deviations from the Gaussian shape and the areas of the peaks representing distances that are not expected to give Gaussian contributions, the validity of approximation (4) can be investigated.

In eqn. (6) given for the radial distribution function the integration is performed for intensity values from $s = 0$ to $s = \infty$. In an electron diffraction experiment, intensity values are only obtained between the limits s_{min} and s_{max}. The omission of the unobservable intensities at the very inner s range (from zero to s_{min}) can be corrected for in two ways. The inner peak of the intensity curve can be calculated theoretically or it can be corrected for on the radial distribution curve by drawing in an "envelope". In this investigation the last method was used. The factor $\exp(-ks^2)$ of the modification functions (3) is effective for eliminating the termination effect due to lack of intensity data

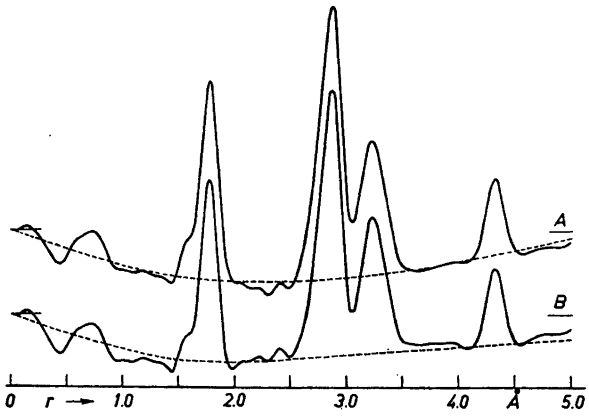

Fig. 2. Hexachloroethane. Radial distribution curves ($k = 0.0009$) with envelopes plotted in. A: modification function $\varphi_3(s)$ used, B: modification function $\varphi_2(s)$ used.

from $s = s_{max}$ to ∞. In this investigation the k-values 0 and 0.0009 Å^2 were used.

Fig. 2 shows two radial distribution curves based on intensity functions modified by $\varphi_2(s)$ and $\varphi_3(s)$, respectively. The envelopes are also shown in Fig. 2 and the damping constants for both curves is $k = 0.0009$ Å^2. Figs. 3 and 4 show the two curves after subtraction of the envelope.

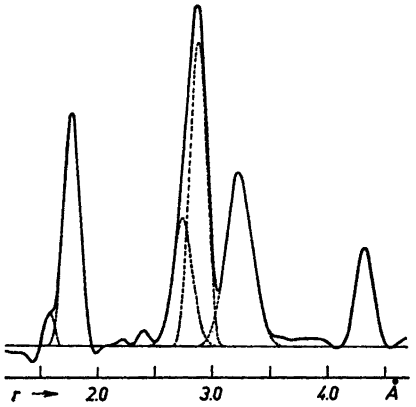

Fig. 3. Hexachloroethane. Radial distribution curve ($k = 0.0009$) with peaks resolved. Modification function $\varphi_2(s)$ used.

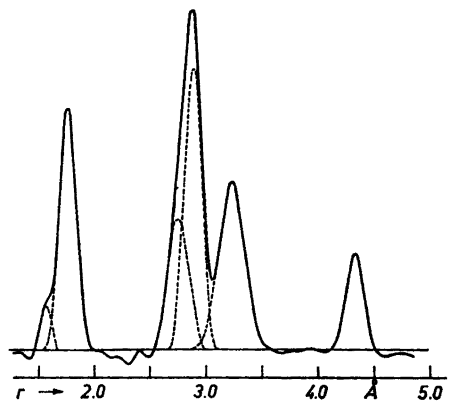

Fig. 4. Hexachloroethane. Radial distribution curve ($k = 0.0009$) with peaks resolved. Modification function $\varphi_3(s)$ used.

The carbon-carbon bond distance peak, which is of special interest for this investigation, is not resolved on the radial distribution curves with damping constant $k = 0.0009$ Å^2 given in Figs. 3 and 4. Two undamped radial distribu-

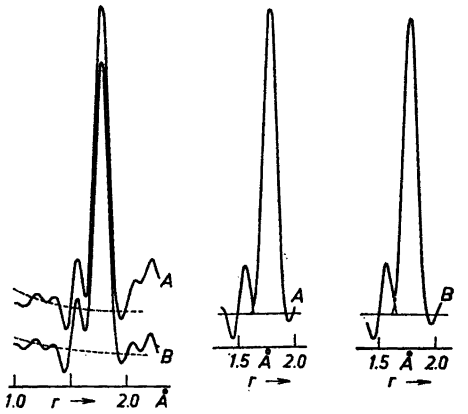

Fig. 5. Hexachloroethane. Undamped radial distribution curves before and after subtraction of the envelopes. A: modification function $\varphi_1(s)$ used, B: modification function $\varphi_2(s)$ used.

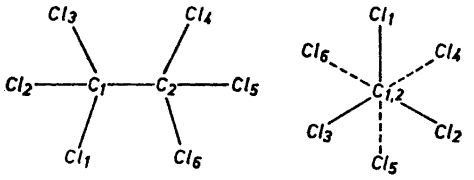

Fig. 6. Numbering of the atoms in the hexachloroethane molecule.

Table 1. Ratio between theoretical and experimental values for areas under the peaks in the radial distribution curves.

	Modification functions used	
Distances	$\varphi_2(s)$	$\varphi_3(s)$
C_1-C_2	114.9	141.2
C_1-Cl_1	124.2	126.4
C_1-Cl_4	129.0	129.2
Cl_1-Cl_2	127.1	127.7
$(Cl-Cl)_g$	126.2	125.9
$(Cl-Cl)_t$	126.3	129.2

tion functions were therefore computed, using the modification function $\varphi_1(s)$ and $\varphi_2(s)$, respectively. Fig. 5 shows the inner parts of the two radial distribution curves with the envelopes plotted in, and the same curves after subtraction of the envelopes.

The weight function Z_C' was determined from the radial distribution curves given in Figs. 3 and 4 by choosing $Z_{Cl}' = Z_{Cl} = 17$, and Z_C' was determined from the two $\sigma(r)/r$-curves to be 7.83 and 8.85, respectively. Calculations of the theoretical areas were based on these values. Table 1 gives the ratio, on an arbitrary scale, between the areas of the theoretical and experimental peaks on the radial distribution curves shown in Figs. 3 and 4. The numbering of the atoms in the first column of Table 1 is shown in Fig. 6.

For both curves the correspondence between theoretical and experimental areas is good except for the C—C distance. The discrepancy can be due to difficulties of resolving the peak complex representing the C—C and C—Cl bond distances and to the fact that a small error in the value of Z_C' will produce a relatively large error in the theoretical area calculated.

The experimentally determined internuclear distances are presented in Table 2. The correspondence between results obtained from the various radial distribution curves is good, and the mean values are listed in column 6.

The carbon-carbon bond distance can also be determined indirectly by making use of the various non-bonded distances in the molecule. When the mean values listed in Table 2 column 6, were used for the non-bonded distances, the following values for the carbon-carbon bond distance were determined:

1.554 Å on the basis of the $(Cl\text{--}Cl)_g$-distance
1.561 Å » » » » » $(Cl\text{--}Cl)_t$- »
1.573 Å » » » » » $C_1\text{--}Cl_4$- »

(The results depend on the values for the $C_1\text{--}Cl_1$ and $Cl_1\text{--}Cl_2$ distances since the determination of the molecular angles are based on these values.)

The last C—C bond distance value is probably the least reliable one since the $(Cl-Cl)_g$ and $(Cl-Cl)_t$ distances were determined from well-resolved peaks, while the C_1-Cl_4-distance was determined from the peak complex composed of the C_1-Cl_4 and Cl_1-Cl_2 distances. The peak complex was resolved by a correlation procedure. If shrinkage effects are taken into account the values given above for the C—C bond distance have to be increased by a small amount.

Table 2. Experimentally determined internuclear distances in hexachloroethane (in Å).

Distances	Modification functions and k-values used				
	$\varphi_3(s)$ $k = 0.0009$	$\varphi_2(s)$ $k = 0.0009$	$\varphi_2(s)$ $k = 0$	$\varphi_1(s)$ $k = 0$	Mean
C_1-C_2	1.567	(1.576)	1.564	1.561	1.564
C_1-Cl_1	1.769	1.769	1.768	1.769	1.769
C_1-Cl_4	2.742	2.740			2.741
Cl_1-Cl_2	2.880	2.877			2.879
$(Cl-Cl)_g$	3.225	3.227			3.226
$(Cl-Cl)_t$	4.328	4.329			4.329

Table 3. Experimentally determined root-mean square deviations from equilibrium internuclear distances (u-values in Å).

Distances	Modification functions and k-values used				
	$\varphi_3(s)$ $k = 0.0009$	$\varphi_2(s)$ $k = 0.0009$	$\varphi_2(s)$ $k = 0$	$\varphi_1(s)$ $k = 0$	Mean
C_1-C_2				0.037	0.037
C_1-Cl_1		0.057	0.060		0.059
C_1-Cl_4		0.069			0.069
Cl_1-Cl_2	0.066				0.066
$(Cl-Cl)_g$	0.101				0.101
$(Cl-Cl)_t$	0.065				0.065

The experimentally determined root-mean-square deviations from the equilibrium internuclear distances (u-values) are listed in Table 3.

A theoretical intensity curve, based on the parameters listed in Table 2 and Table 3 (mean values), was computed and Fig. 7 shows a comparison be-

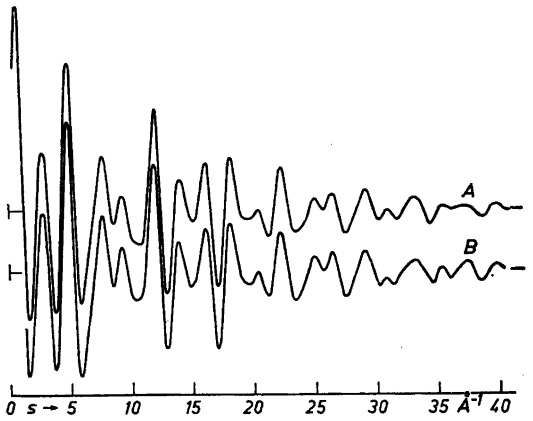

Fig. 7. Hexachloroethane. Theoretical (A) and experimental (B) intensity curves.

tween the experimental and theoretical intensity curves. The correspondence is found to be very satisfactory.

RESULTS

As a result of this investigation the following molecular parameters and corresponding error limits for hexachloroethane can be given:

C—C:	1.564 ± 0.014 Å	u_{CC}:	0.037 ± 0.015 Å
C—Cl:	1.769 ± 0.003 Å	u_{CCl}:	0.059 ± 0.005 Å
∠CCCl:	$110.0° \pm 0.5°$		

The molecule is found to be in the staggered configuration. The experimentally determined internuclear distances and corresponding u-values are listed in Tables 2 and 3. The error limits given above are not standard deviations, but are based on estimates of the precision of the measurements involved. We are aware of the fact that the error estimate is subject to considerable uncertainties.

DISCUSSION OF THE RESULTS

The main purpose of this investigation was to study the influence of highly electronegative substituents on the length of the carbon-carbon single bond distance. Hexachloroethane was chosen because it serves as a good example of molecules of the mentioned type and because earlier structure determinations of the molecule disagree seriously.

The carbon-carbon bond length in hexachloroethane is determined to be 1.564 ± 0.014 Å, a value that is definitely larger than the C—C distance in the ethane molecule (approximately 1.536 Å). The bond lengthening might be due to repulsions between the negatively charged chlorine atoms and also to van der Waals repulsions between the chlorine atoms. The $(Cl—Cl)_{gauche}$ distance in this investigation was determined to be 3.226 Å while the sum of the van der Waals radii for the two chlorine atoms is 3.60 Å. One might explain the long C—C distance in C_2Cl_6 by assuming that it is less energy-consuming for the molecule to overcome the repulsion energies by mainly stretching the carbon-carbon bond rather than by stretching all the carbon-chlorine bonds.

The carbon-carbon bond distance agrees with that found by Karle *et al.*[5] ($1.57^{+0.10}_{-0.07}$ Å), but disagrees with the results of Morino *et al.*[6] ($1.49_9^{+0.05}_{-0.03}$ Å). The latter investigators found that the distance in question probably is shorter than the ethane C—C distance, but their error limits were too large to give unambiguous results. The s-range of the intensity data of their work covered only half the s-range of this investigation. This fact might be responsible for the deviating results.

For the C—Cl bond distance this investigation gave the value 1.769 ± 0.003 Å while Karle *et al.* and Morino *et al.* obtained the values 1.74 ± 0.01 Å and $1.76_3 \pm 0.020$ Å, respectively. The result of this investigation is in accordance with Morino's C—Cl bond distance determination but disagrees with that of Karle *et al.*[1]

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REFERENCES

1. Sasada, Y. and Atoji, M. *J. Chem. Phys.* **21** (1953) 145.
2. Hassel, O. and Viervold, H. *Acta Chem. Scand.* **1** (1947) 149.
3. Kimura, M. and Morino, Y. *J. Chem. Soc. Japan* **68** (1947) 78.
4. Morino, Y. and Iwasaki, M. *J. Chem. Phys.* **17** (1949) 216.
5. Swick, D. A., Karle, I. L. and Karle, J. *J. Chem. Phys.* **22** (1954) 1242.
6. Morino, Y. and Hirota, E. *J. Chem. Phys.* **28** (1958) 185.
7. Almenningen, A., Bastiansen, O. and Fernholt, L. *Kgl. Norske Videnskab. Selskabs Skrifter* **1958** No. 3.

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