The Molecular Structure of Hexachlorobenzene by Electron Diffraction

By Takahide SAITO

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An early electron diffraction investigation of the structure of haxachlorobenzene by the usual visual method was reported by Brockway and Palmer¹⁾, observing the scattering in a range of q* less than 60 and using the trial and error method, led to the conclusion that the molecule has the planar configuration as a whole. In contrast with their opinion, Bastianssen and Hassel²⁾ re-investigated the molecule by the sector method and reported that the non-planar structure, illustrated in Fig. 1, is supported on the basis of interpretation of the peaks in the radial distribution curve, but they did not apply the trial and error method to their investigations. The above contradictory results are compared in Table 1, containing the distances of the principal atomic pairs**. Although it is generally recognized that the sector method is superior to the visual method, it is not perfectly meaningless to re-investigate the molecule by the visual method and the trial and error process, if it is possible to obtain the photographs with rings extending to higher scattering angle, that is, if it is possible to observe the rings of larger q values than the previous reports.

Experimental

The apparatus of electron diffraction is the same as that in the previous reports³⁾ and the diffraction can be easily observed over the broad range of q. The electron wavelength, about 0.055 Å, was calibrated with gold foil diffraction. The sample was prepared by Holleman's method⁴⁾, m. p. 227°C. Measurements of the photographs were carried out by the usual visual method.

TABLE I. A COMPARISON OF TWO REPORTS

Investigater	θ	C–Cl	C′–Cl	C″–Cl	Cl–Cl	Cl′–Cl
Brockway, Palmer	0	1.70	2.69	4.00	3.11	5.39
Bastianssen, Hassel	12	1.72	2.68	3.99	3.15	5.39

The unit of interatomic distance is Å.
θ is the angle between the direction of C–Cl and the benzene plane.

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1) L. O. Brockway and K. J. Palmer, *J. Am. Chem. Soc.*, **59**, 2181 (1937).

2) O. Bastianssen and O. Hassel, *Acta Chem. Scand.*, 1, 489 (1947).

* $q=(10/\pi)s$, $s=(4\pi/\lambda)\sin\theta/2$, which λ is the wavelength.

** The term "principal" is used for the atomic pair having the larger values of nZZ/r, in which n is the number of the pair, Z is the atomic number and r is the length of atomic pair.

3) T. Yuzawa and M. Yamaha, This Bulletin, **26**, 414 (1953).

4) M. Holleman, *Rec. trav. chim.*, **39**, 763 (1920).

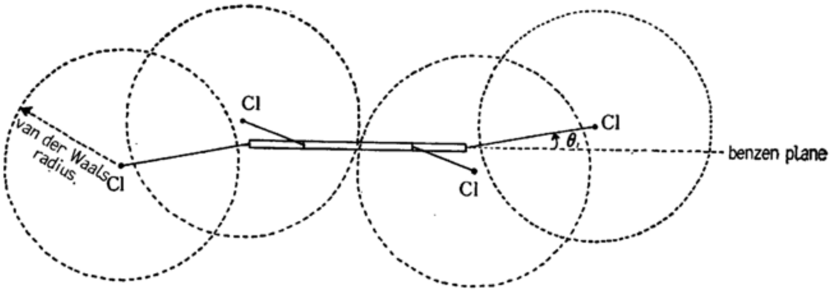

Fig. 1. The schema of deviation of Cl atoms from the benzene plane.

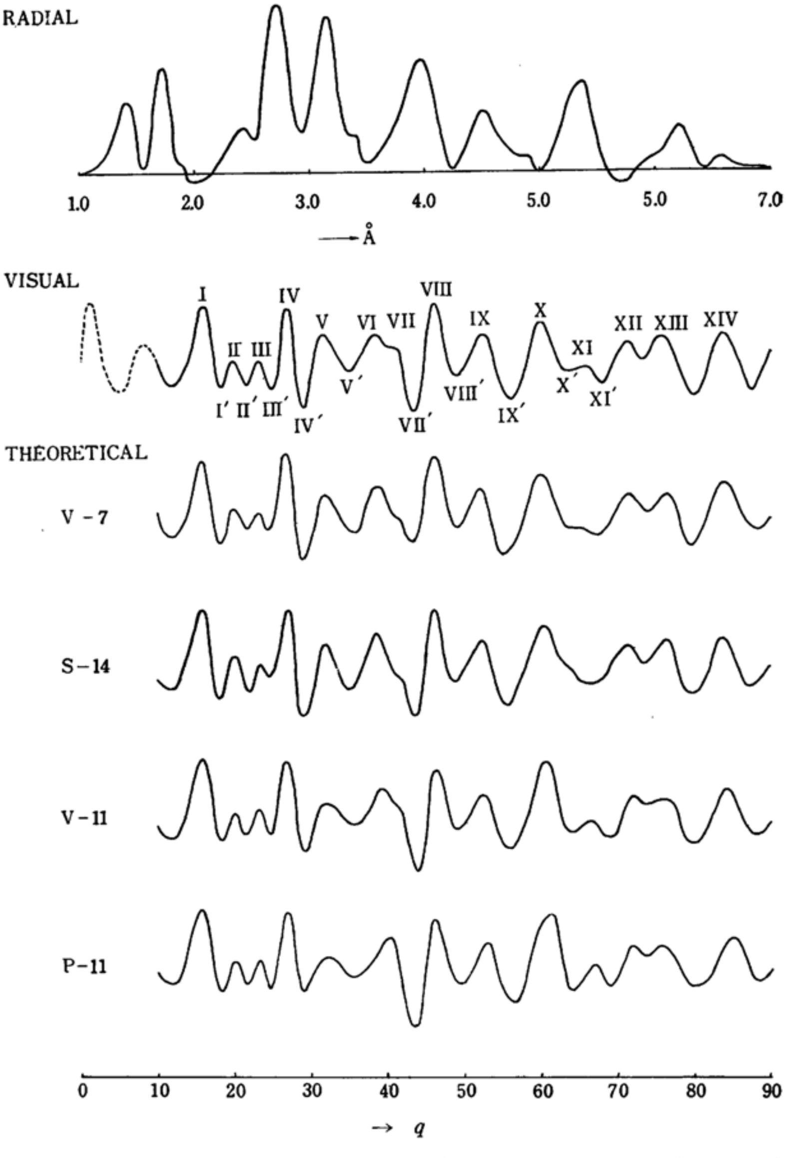

Fig. 2. The radial distribution curve, visual curve and various theoretical curves.

Procedure and Results

The experimental visual curve is shown in Fig. 2: fourteen maxima and ten minima have been observed in the range of q from 15 to 95. From the visual intensity curve, the radial distribution curve has been calculated according to the equation[5)]

$$rD(r)=\sum_{q=1}^{q_{\max}} I(q)\exp(-aq^2)\sin(\pi qr/10)$$

$$\exp(-aq^2_{\max})=0.1$$

$$q=(10/\pi)s \qquad s=(4\pi/\lambda)\sin(\theta/2)$$

in which θ is the scattering angle and a is a constant. The radial curve shows remaining ghosts, but has clearly six principal peaks at 1.40, 1.72, 2.70, 3.99, 3.15 and 5.36 Å. They correspond to the interatomic distances of C–C, C–Cl, C′–Cl, C″–Cl, Cl–Cl and Cl′–Cl, respectively.

Theoretical intensity curve for the molecular models have been calculated by the use of the equation[5)]

$$I(q)=\sum_i\sum_j (Z_iZ_j/r_{ij})\exp(-a_{ij}q^2)\sin(\pi qr_{ij}/10)$$

$$a_{ij}=(\pi^2/200)l^2_{ij}$$

where l_{ij} is the mean amplitude of the atomic distance r_{ij}. The coefficients of thermal vibration, a_{ij}, roughly estimated in reference to the calculated aliphatic data[6-8)] is introduced into each model, for $q>30$. The values of coefficients are shown in Table II. The theoretical curves were calculated to cover the following ranges of the principal parameters: C′–Cl=2.66∼2.72 Å, C″–Cl=3.94∼4.02 Å, Cl–Cl=3.06∼3.17 Å and Cl′–Cl=5.30∼5.42 Å. In Fig. 2 are shown some of the theoretical curves, which agree comparatively well with the visual intensity curve and have the close

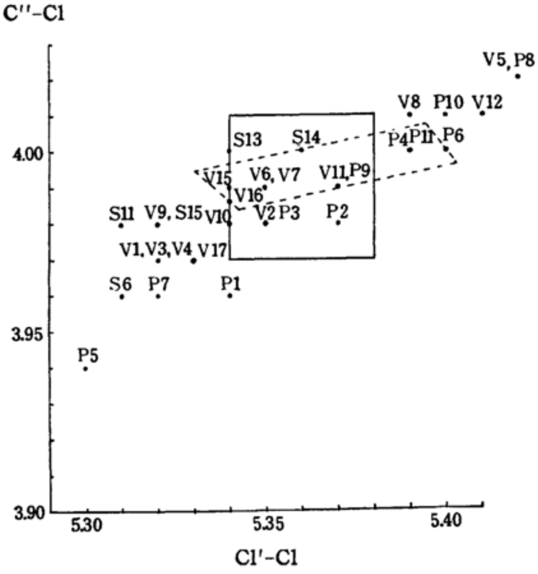

Fig. 3. The parameter chart of C″-Cl vs. Cl′-Cl.

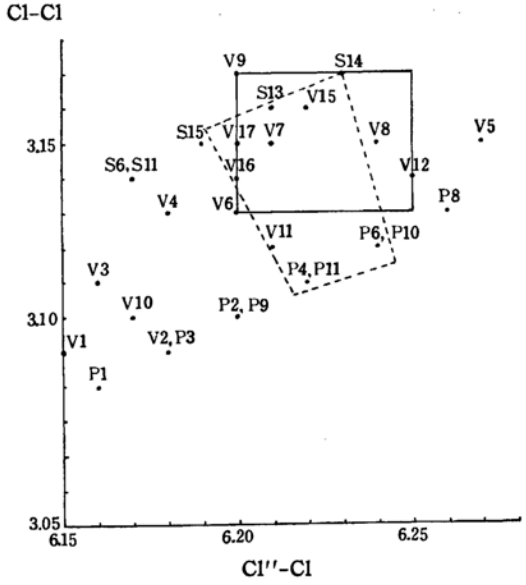

Fig. 4. The perameter chart of Cl-Cl vs. Cl″-Cl

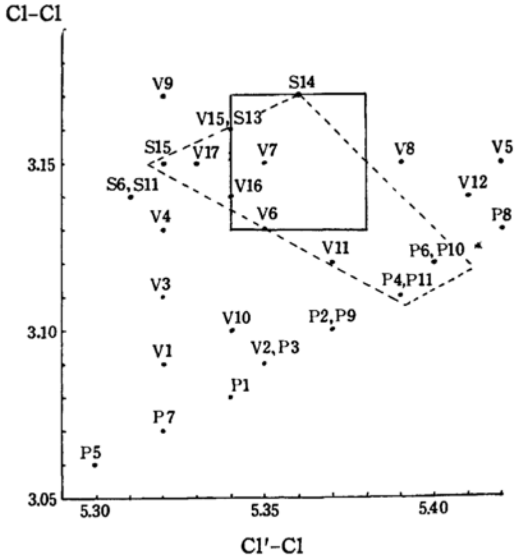

Fig. 5. The parameter chart of Cl-Cl vs. Cl′-Cl.

[5)] R. Spurr and V. Schomaker, *J. Am. Chem. Soc.*, **64**, 2693 (1942).

[6)] J. Karle, *J. Chem. Phys.*, **20**, 65 (1952).

[7)] Y. Morino, K. Kuchitsu and T. Shimanouchi, ibid., **20**, 726 (1952).

[8)] Y. Morino, K. Kuchitsu, A. Takahashi and K. Maeda, ibid., **21**, 1927 (1953).

TABLE II. THE COEFFICIENTS OF THERMAL VIBRATION TERMS

Atomic pair	a_{ij}	Atomic pair	a_{ij}
C–C	0	C′′–Cl	0.00022
C′–C	0.00007	C–Cl	0.00033
C′′–C	0.00015	Cl–Cl	0.00011
C–Cl	0	Cl′–Cl	0.00046
C′–Cl	0.00008	Cl′′–Cl	0.00062

TABLE III. RESULTS OF QUOTED MODELS AND RADIAL DISTRIBUTION CURVE

Atomic pair	Model number				Radial
	V-7	S-14	P-11	V-11	
C–Cl	1.72	1.72	1.70	1.71	1.72
C–Cl	2.70	2.70	2.69	2.70	2.70
C–Cl	3.99	3.99	4.00	3.99	3.99
Cl–Cl	3.15	3.16	3.11	3.12	3.15
Cl–Cl	5.35	5.34	5.39	5.37	5.36
Av. of q_{calc}/q_{obs}	1.001	0.996	1.005	1.005	
Mean deviation	0.008	0.008	0.016	0.005	

V-7, S-14 and V-11 are the non-planar models. P-11 is the plane model.

values of parameters to those of the interatomic distances from the radial distribution curve.

The values of principal parameters of models are shown in Table III. No distinct differences in the theoretical curves to contribute to any decisive choice can be observed, and the observable, relatively small, difference are as follows: (1) the relative shapes and positions of max. V—VII; (2) the relationships of max. VI and min. XI. The theoretical curves of the non-planar models show the good agreements rather than the curves of the plane models in the shapes of the above respects and in the values of q_{calc}/q_{obs} and of interatomic distances.

Summary

The non-planar structure of hexachlorobenzene is fairly suitable rather than the planar structure and the values of principal interatomic distances are

$$\text{C–Cl} = 1.72 \pm 0.01\ \text{Å}$$

$$\text{C}'\text{–Cl} = 2.69 \pm 0.02\ \text{Å}$$

$$\text{Cl–Cl} = 3.15 \pm 0.02\ \text{Å}$$

They are in agreement with Hassel's data.

The author thinks that the re-investigation of the molecular structure of hexachlorobenzene by the precise sector method is necessary.

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Department of Chemistry
Faculty of Science
Tokyo University of Education
Koishikawa, Tokyo