

## Electron Diffraction Investigation of $\alpha$ , $\beta$ , $\gamma$ , $\delta$ and $\varepsilon$ Benzene Hexachloride

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According to the older conception 1,2,3,4,5,6-hexachlorocyclohexane may occur in eight different forms as far as optically active modifications are not taken into consideration. Only one of these forms, however, should be separable into optically active antipodes. The modern picture based on a non-planar carbon ring and the possibility of a conversion of the carbon ring does not alter this result although it deviates in essential features from the older one<sup>1,2</sup>. At present *five* of the eight benzene hexachlorides are known and we have thought it worth while to try to determine the molecular configurations of all these substances in the vapour state using the electron diffraction sector method.

The final results of our investigation has already been published in a condensed form<sup>3</sup>. We feel, however, that a more detailed report should be given, and the present paper therefore brings the experimentally obtained distribution curves and the discussion leading us to the conclusions already published.

We want first, however, to draw the attention to the circumstance that each molecular species may exist in two forms, generally different, which are transformed into each other by a conversion of the carbon ring. In those cases in which the energy of these two forms of a benzene hexachloride is different, the interaction of atoms not directly linked together will probably suffice to make the concentration of the less stable form in the vapour practically equal to zero.

The results obtained are summarized in Table 1 and Fig. 1.

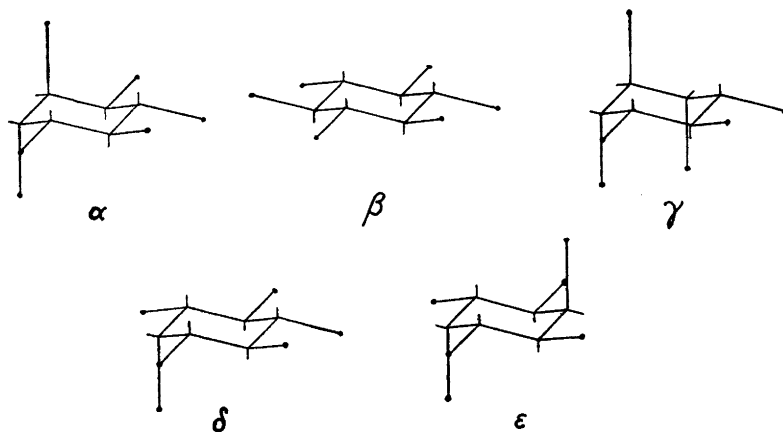


Fig. 1. Configurations of the five isomers.

Table 1. Configuration of isomers of benzene hexachloride.

Isomer	Configuration
$\alpha$	$\varepsilon \varepsilon \kappa \kappa \kappa \kappa$
$\beta$	$\kappa \kappa \kappa \kappa \kappa \kappa$
$\gamma$	$\varepsilon \varepsilon \varepsilon \kappa \kappa \kappa$
$\delta$	$\varepsilon \kappa \kappa \kappa \kappa \kappa$
$\varepsilon$	$\varepsilon \kappa \kappa \varepsilon \kappa \kappa$

In order to demonstrate the way leading us to these conclusions we start with an inspection of the  $\frac{\sigma(r)}{r}$  curves of the five isomers (Fig. 2). It will be observed that these five experimental curves are indeed strikingly similar, all showing seven rather pronounced peaks (I to VII). The  $r$ -values of the first four peaks are nearly identical, but in the case of number V (occurring approximately at  $r = 4.7 \text{ \AA}$ ) a shift of the  $\beta$  peak towards a smaller  $r$ -value and the  $\gamma$  peak towards a greater  $r$ -value is observed. The distance responsible for this peak in the  $\beta$  compound is  $C_1-Cl_{4\kappa}$ , whereas in the other compounds distances corresponding to greater  $r$ -values ( $Cl_{1\kappa}-Cl_{3\varepsilon}$  and  $Cl_{1\kappa}-Cl_{4\varepsilon}$ ) will also occur. The  $\gamma$  compound contains the greatest number of  $\varepsilon$ -Cl-atoms and consequently the  $r$ -value of peak V should be greatest for this substance.

The position of peak VI ( $r \approx 5.45 \text{ \AA}$ ) is nearly the same in all the  $\frac{\sigma(r)}{r}$ -curves, but the height is markedly different for the five substances. The

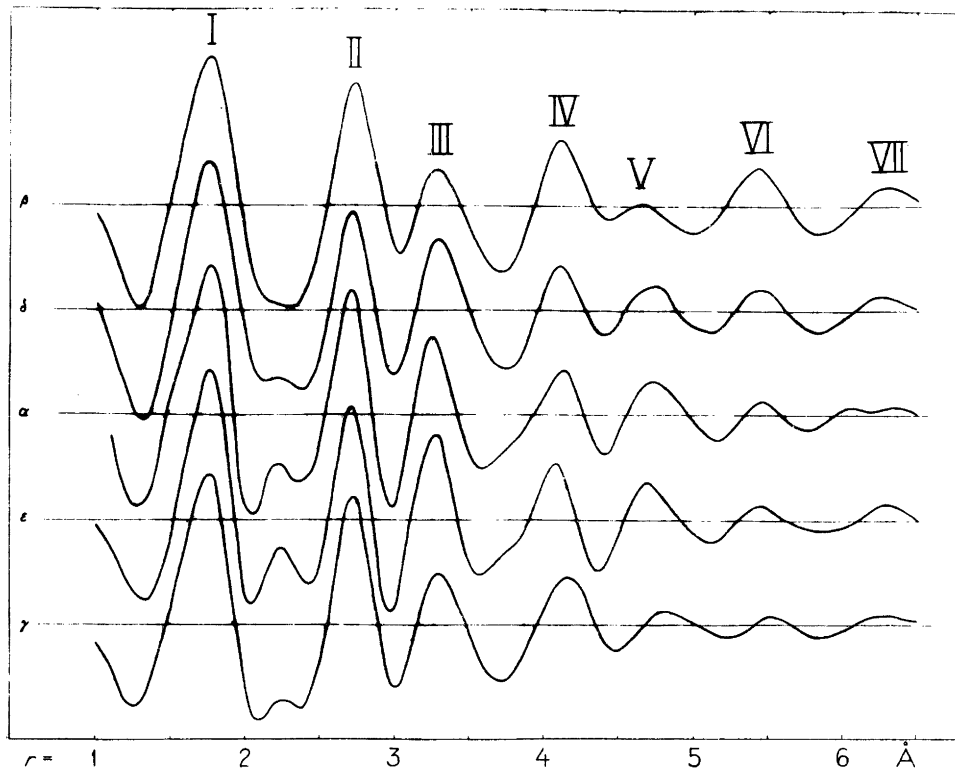


Fig. 2. Experimental  $\frac{\sigma(r)}{r}$ -curves of the five isomers.

internuclear distance responsible for this peak is  $\text{Cl}_{1x}-\text{Cl}_{3x}$  and consequently the expected relative heights of this peak are:

$$6(\beta), \quad 4(\delta), \quad 2(\alpha), \quad 2(\epsilon), \quad 1(\gamma)$$

From Fig. 1 it is seen that the heights are indeed decreasing from  $\beta$  to  $\gamma$ , those of  $\alpha$  and  $\epsilon$  being almost equal:

$$\beta > \delta > \alpha \approx \epsilon > \gamma$$

The peak just discussed (VI) is especially well suited as a basis for comparison because it is no doubt caused by the  $\text{Cl}_{1x}-\text{Cl}_{3x}$  distance with almost negligible disturbances caused by other distances.

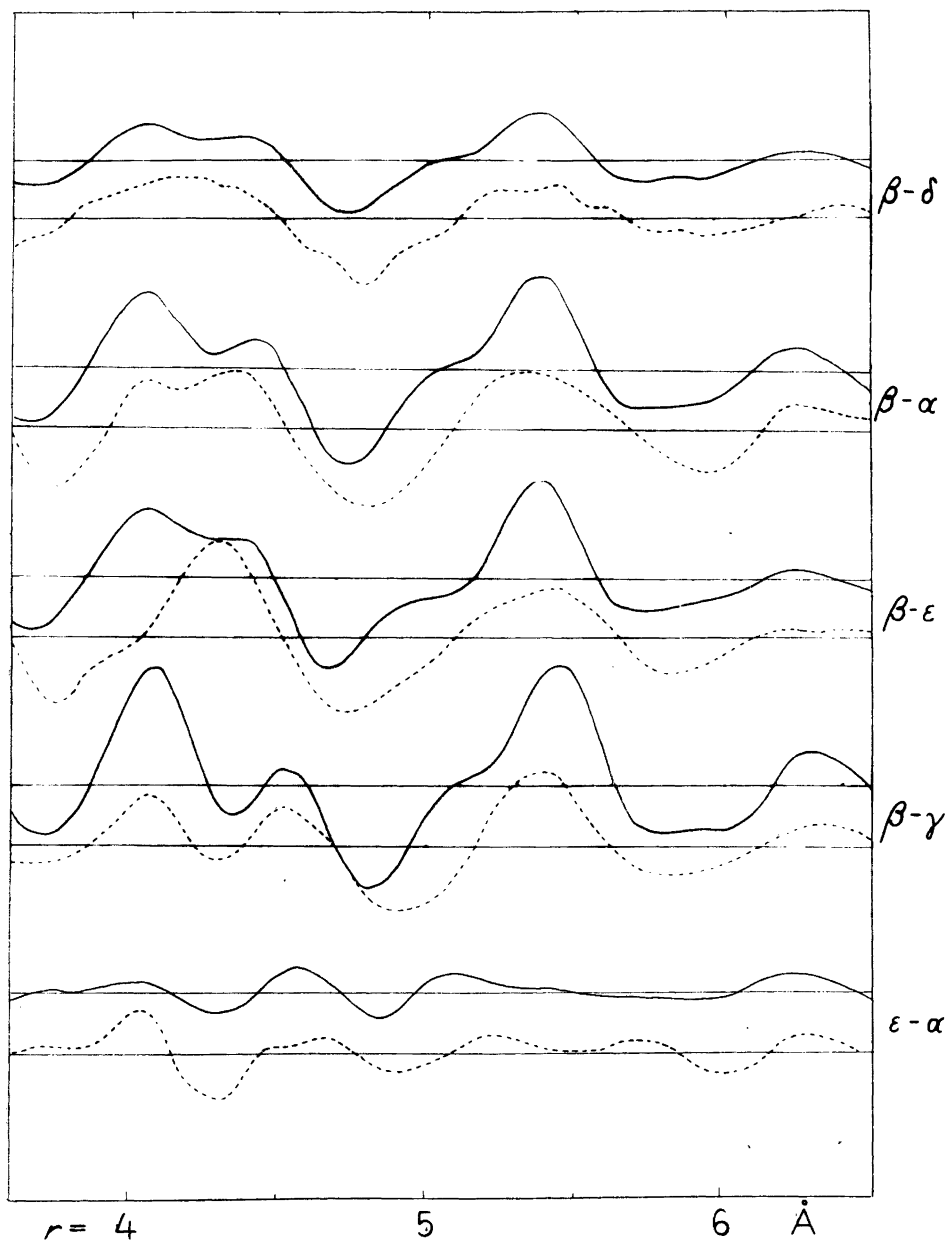


Fig. 3. Differential  $\frac{\sigma(r)}{r}$ -curves. Fully drawn curves are theoretical curves, dotted curves experimental ones.

Peak VII (due to the distance  $\text{Cl}_{1\kappa}-\text{Cl}_{4\kappa}$ ) should be expected to be most pronounced in the case of the  $\beta$  isomer, the  $\delta$  and  $\epsilon$  isomers follow with the same weight factor, and the height should be still smaller for the  $\alpha$  compound and the peak disappear for the  $\gamma$  compound. This is generally in good agreement with the heights observed in the experimental curves.

The most valuable informations, however, may be obtained when comparing differential  $\frac{\sigma(r)}{r}$ -curves — experimental and theoretical — each differential curve referring to a given pair of isomers. This procedure has the advantage that the contribution to the curve under discussion from a considerable number of internuclear distances occurring in both substances is automatically eliminated and the effects of distances which are different in the two substances are being accentuated. In the inner part of the differential curves ( $r < \text{about } 3.6 \text{ \AA}$ ) the amplitudes of the  $\frac{\sigma(r)}{r}$ -curves are comparatively great and here an error in one of the experimental curves will have more serious consequences for the resulting differential curve than a corresponding relative error will have in the outer part of the  $\frac{\sigma(r)}{r}$ -curve.

We have chosen the  $\beta$  compound as a standard substance of reference because the configuration of this substance may be regarded as definitively settled, and because it contains  $\kappa$ -Cl atoms only. In Fig. 3 the experimental and theoretical differential curves are reproduced in the following order: ( $\beta-\delta$ ), ( $\beta-\alpha$ ), ( $\beta-\epsilon$ ), ( $\beta-\gamma$ ) and as a supplement ( $\epsilon-\alpha$ ). The theoretical curves have been calculated putting  $\text{C}-\text{C} = 1.54 \text{ \AA}$ ,  $\text{C}-\text{Cl} = 1.76 \text{ \AA}$ , and assuming normal tetrahedral structures based on the symmetrical form of the carbon ring.

It is seen that the correspondance between theoretical and experimental curves is at least as good as might be expected. It must be admitted, however, that the ( $\beta-\alpha$ )- and ( $\beta-\epsilon$ )-curves are so similar that a final distinction between the  $\alpha$  and  $\epsilon$  isomers cannot be based on these curves only. This is the reason why we have included the ( $\epsilon-\alpha$ )-curves in our discussion. It is obvious from these curves that the  $\epsilon$  and  $\alpha$  isomers cannot be interchanged without totally spoiling the agreement between experimental and theoretical ( $\epsilon-\alpha$ )-curves.

Our investigation was of course not carried out without considering the possible configurations so far not mentioned in this paper:

$\epsilon \kappa \epsilon \kappa \kappa \kappa$

$\epsilon \epsilon \kappa \epsilon \kappa \kappa$

$\epsilon \kappa \epsilon \kappa \epsilon \kappa$

We have not been able, however, to obtain agreement between our experimental curves and the theoretical ones assuming any one of these configurations to be represented by one of the five substances under investigation.

It is of course of interest to examine the deviations from ideal structures actually occurring in the series of benzene hexachlorides. Most convenient for this purpose is of course the symmetrical  $\beta$  compound which contains only  $\alpha$ -chlorine atoms and no  $\varepsilon$  bonded chlorine. In this case there is no reason to assume a deformation which would diminish the symmetry of the molecule. The  $\text{Cl}_{1\alpha}\text{—Cl}_{2\alpha}$ -distance of the ideal structure, however, would be somewhat smaller than those expected to be energetically favourable. We have therefore calculated the internuclear distances in a series of symmetrical models in which the  $\text{C—C—Cl}$ - and  $\text{C—C—C}$ -angles are different from  $109.5^\circ$ . The most satisfactory agreement between calculated distances and distances given by the positions of the maxima of the  $\frac{\sigma(r)}{r}$ -curve was obtained with a  $\text{C—C—C}$ -angle equal to  $114^\circ$  and a  $\text{C—C—Cl}$ -angle of  $112^\circ$  (Table 2).

Table 2. Atomic distances in  $\beta$  isomer.

Type of distance	Exp.	Theoretical (ideal structure)	Theoretical (deformed)
$\text{C}_1\text{—Cl}_1$	1.76	1.76	1.76
$\text{C}_1\text{—Cl}_2$	2.73	2.70	2.74
$\text{Cl}_1\text{—Cl}_2$	3.28	3.18	3.25
$\text{C}_1\text{—Cl}_3$	4.12	4.08	4.14
$\text{C}_1\text{—Cl}_4$	4.65	4.56	4.64
$\text{Cl}_1\text{—Cl}_3$	5.44	5.39	5.46
$\text{Cl}_1\text{—Cl}_4$	6.33	6.26	6.35

The other benzene hexachlorides all contain  $\varepsilon$ -Cl-atoms and here the  $\text{Cl}_{1\varepsilon}\text{—H}_{3\varepsilon}$ -repulsion — the existence of which has been clearly demonstrated in earlier work on chlorinated cyclohexanes <sup>4</sup> — will no doubt cause the  $\varepsilon\text{—Cl}$ -bonds to be bent away from the principal axis of the carbon ring.

More serious deviations from tetrahedral valency angles must of course occur when two  $\varepsilon$ -chlorine atoms appear in 1,3 position. The  $\gamma$  compound is the only one of the known benzene hexachlorides having such an arrangement, and here the X-ray crystallographic work of Bijvoet and co-workers <sup>5</sup> clearly shows the effect of the  $\text{Cl}_{1\varepsilon}\text{—Cl}_{3\varepsilon}$ -repulsion. Our experimental differential ( $\beta\text{—}\gamma$ )-curve, however, does not demonstrate this effect because it begins with an  $r$ -value of 3.6 Å.

The dipole moments of the five known benzene hexachlorides have been measured by Hetland<sup>6</sup> in our laboratory and the results seem to be in accordance with our configuration determinations. The moments of the  $\beta$  and  $\epsilon$  isomers are zero and the  $\alpha$  and  $\delta$  isomers both have a moment of 2.2 D. The  $\gamma$  isomer has the greatest moment (2.9 D). If we disregard the mutual interaction between the C—Cl bond moments and also the deviations from tetrahedral angles, rough values of the resultant moments may be computed which might be expected to give at least the right sequence of the dipole moment values. We find (Table 3):

Table 3. Dipole moments.

	Exp.	Calc.
$\alpha$	2.2	3.4
$\beta$	0	0
$\gamma$	2.9	4.9
$\delta$	2.2	3.4
$\epsilon$	0	0

As already pointed out<sup>2</sup> the substance which has the  $\epsilon\epsilon\kappa\kappa\kappa\kappa$ -configuration should be the only benzene hexachloride capable of existing in d and l forms. It was therefore very interesting to learn that Cristol<sup>7</sup> has been able to prepare the l form of  $\alpha$  benzene hexachloride.

Dr. L. K. Frevell of the Dow Chemical Company was kind enough to supply us with sufficient of the  $\epsilon$  isomer both for the electron diffraction investigation and for the crystal structure determination. The latter is being carried out by cand.real. N. Norman and is now nearly completed. His results fully confirm the conclusions drawn from the electron diffraction analysis.

When comparing the  $\frac{\sigma(r)}{r}$ -curves of closely related substances and studying differential curves it is important to eliminate — as far as possible — systematic differences in the r-scale due to inaccuracies in measurements of voltage and the effective distance from the point of diffraction to the photographic plate. In the curves reproduced in Fig. 1 a slight adjustment of the abscissa scales have been carried through with the aim of placing the first high peak corresponding to the C—Cl bond distance at exactly the same  $r$ -value, namely 1.76 Å. The  $r$ -values of this maximum in the original curves of the  $\alpha$ ,  $\beta$ ,  $\gamma$ ,  $\delta$  and  $\epsilon$  compounds were 1.79, 1.78, 1.77, 1.77 and 1.80 respectively, giving a mean value of 1.78 Å for the C—Cl-distance. If the true ratio of the C—C and C—Cl bond distances are 1.78 : 1.54 and not 1.76 : 1.54, the deviations from tetra-

hedral valency angles in the  $\beta$  compound would be a little larger than those indicated above.

The absolute heights of the peaks in the  $\frac{\sigma(r)}{r}$ -curves depend to some degree upon the time of exposure, the photographic material used and the drawing of the background in the intensity curves. In order to obtain ordinate values suited for a direct comparison of the  $\frac{\sigma(r)}{r}$ -curves of the different isomers and the evaluation of differential curves, the ordinate scales were so adjusted, that the height of the first pronounced peak at  $r = 1.76 \text{ \AA}$  was the same in all cases. The number of C—Cl bonds being the same for all the isomers we think that such a procedure should be the most satisfactory in the present case.

#### SUMMARY

The configurations of the five known isomers of benzene hexachloride have been studied in the vapour phase by the electron diffraction sector method. The distance distribution curves ( $\frac{\sigma(r)}{r}$ -curves) of these five isomers are very similar because the greater part of the internuclear distances are nearly identical in all the molecules in question. A careful examination of the curves, however, and the study of a selected set of differential curves has made it possible to decide which configuration corresponds to each of the individual isomers. The general types of deformations caused by repulsive forces acting between atoms not directly linked together and resulting in deviations from tetrahedral valency angles are discussed.

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