

Electron Diffraction Investigation of α , β , γ , δ and ϵ Benzene Tetrachloride

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The structure of the five isomers of benzene tetrachloride (BTC) isolated by Calingaert, Kolka, Orloff *et al.* at the Research Laboratories of Ethyl Corporation, Detroit, have been studied by pure chemical means by the Ethyl Corporation team^{1,2} and by dipole moment measurements at this institute³. To obtain a direct and conclusive determination of the structure of these five isomers the present electron diffraction work based on the rotating sector method was started.

The electron diffraction diagrams of the five isomers were all very similar. By visual inspection we were not able to distinguish between the diagrams of the α , β , γ and ϵ isomers; however, the diagrams of the δ isomer could easily be separated from the other ones. In Fig. 1 the intensity curves for the five isomers are given. The curves are multiplied by the usual modification factors⁴.

The $\frac{\sigma(r)}{r}$ curves calculated by Fourier transformation are given in Fig. 2.

The curves have been normalized so that the peaks having their maximum at 2.73 Å are of the same height for all curves. The inner parts of the curves are practically identical as might be expected. The outer parts of the curves, however, are markedly different. The inner parts of the curves give the average carbon carbon bond distance, the carbon chlorine bond distance and the average values for the distances of the type C₂-Cl₃. The corresponding peaks have their maximum values at 1.50, 1.80 and 2.73 Å respectively, suggesting the following values for the structure parameters: C = C distance 1.35 Å, C-C distance 1.54 Å, C-Cl distance 1.80 Å and the average C-C-Cl angle 109.5°. The distances corresponding to the peak at 2.73 Å might to some extent be split up particularly for less symmetric molecules. For the δ isomer this peak is somewhat higher compared to the peak at 1.80 Å than for the other isomers. This might be related to the assumption of a high symmetry for the δ isomer.

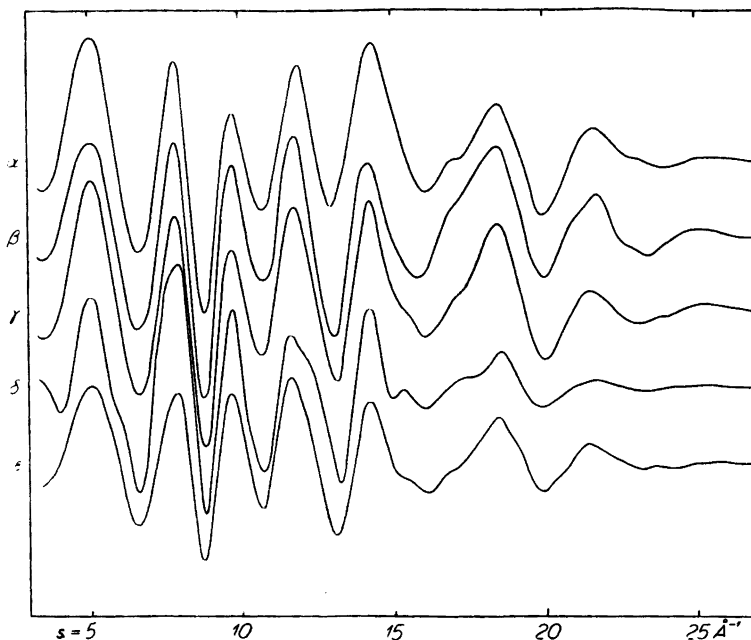


Fig 1. Intensity curves of α , β , γ , δ and ϵ BTC.

Adopting the ideas and designations used for cyclohexane derivatives⁵ the possible configurations of the BTCs can be characterized by the scheme given in Table 1.

Table 1. Possible structure forms for the BTCs.

I	$\kappa \kappa \kappa \kappa \rightleftharpoons \epsilon \epsilon \epsilon \epsilon$
II	$\epsilon \kappa \kappa \kappa \rightleftharpoons \kappa \epsilon \epsilon \epsilon$
III	$\kappa \epsilon \kappa \kappa \rightleftharpoons \epsilon \kappa \epsilon \epsilon$
IV	$\epsilon \epsilon \kappa \kappa \rightleftharpoons \kappa \kappa \epsilon \epsilon$
V	$\epsilon \kappa \kappa \epsilon \rightleftharpoons \kappa \epsilon \epsilon \kappa$
VI	$\epsilon \kappa \epsilon \kappa \rightleftharpoons \kappa \epsilon \kappa \epsilon$

The $\frac{\sigma(r)}{r}$ curves of the five isomers exclude $\epsilon \epsilon \epsilon \epsilon$ and $\kappa \epsilon \epsilon \epsilon$ as possible forms for any of the known isomers. Even if rather marked deformations from ideal structures are assumed the $\frac{\sigma(r)}{r}$ curves of these two forms should have a pronounced peak at an r -value of approximately 4.3 Å. None of the experi-

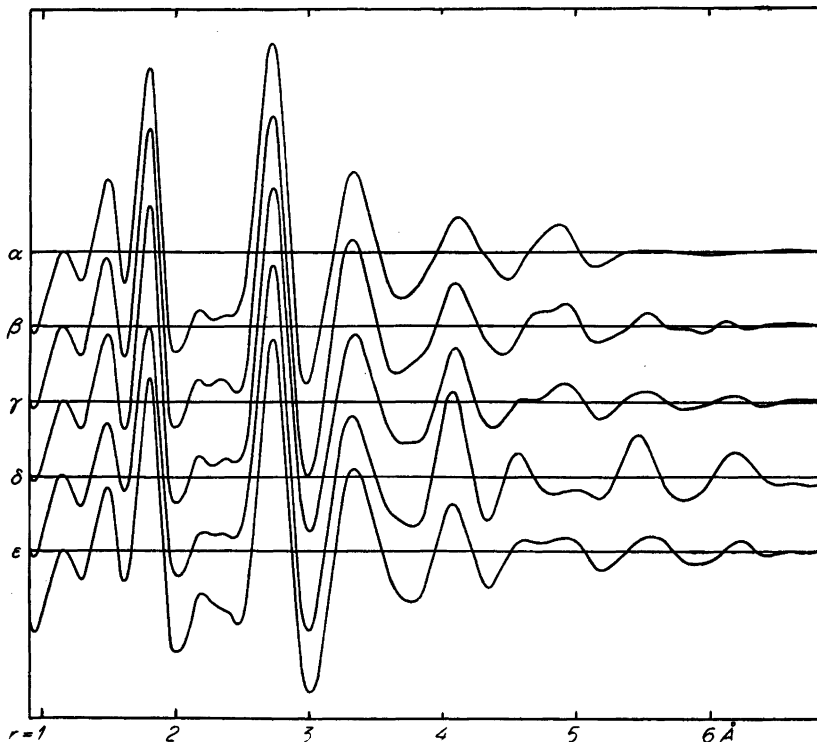


Fig. 2. $\frac{\sigma(r)}{r}$ curves of α , β , γ , δ and ϵ BTC.

mental $\frac{\sigma(r)}{r}$ curves exhibits such a peak. (Minor contribution of these forms to an equilibrium of the kind indicated in Table 1 can of course not be excluded by this argument.)

By inspection of the $\frac{\sigma(r)}{r}$ curves the δ isomer can easily be identified with the $\kappa\kappa\kappa\kappa$ form. The peaks at 4.12, 4.57 and 5.45 Å of the $\frac{\sigma(r)}{r}$ curve of the δ isomer are higher than the corresponding peaks of any of the other isomers. This should indeed be the case for the $\kappa\kappa\kappa\kappa$ form. The lack of the peak at about 4.9 Å is also a characteristic feature of the $\frac{\sigma(r)}{r}$ curve of the δ isomer. Beside the $\kappa\kappa\kappa\kappa$ form the $\epsilon\kappa\epsilon\kappa$ form is the only one not excluded for other reasons that should be expected to lack the peak at about 4.9 Å. This fact should therefore be an argument for excluding the $\epsilon\kappa\epsilon\kappa$ form. Experiences

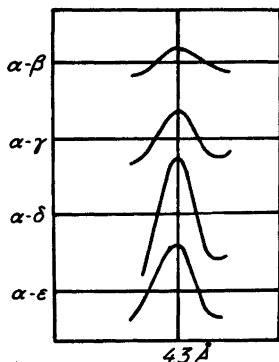


Fig. 3. $\frac{\sigma(r)}{r}$ difference curves in the region of r equal to 4.3 Å.

from chlorinated cyclohexanes are in accordance with this result as the presence of $1\varepsilon-3\varepsilon$ chlorine atoms seems to be less favourable⁶.

The next isomer to be studied is the α isomer. The lack of peaks on the $\frac{\sigma(r)}{r}$ curve beyond r equal to 5 Å makes us believe that this isomer has the form $\varepsilon\varepsilon\kappa\kappa$. All the other forms of Table 1 not yet excluded require maxima beyond this point. To obtain further evidence we have calculated the $\frac{\sigma(r)}{r}$ difference curves in the neighbourhood of $r = 4.3$ Å. This r -value corresponds to the $1\varepsilon-2\varepsilon$ distance which should occur for the following three forms not yet excluded: $\varepsilon\varepsilon\kappa\kappa$, $\kappa\varepsilon\varepsilon\kappa$ and $\varepsilon\kappa\varepsilon\varepsilon$. (The last one of these forms will be excluded as we shall see later on). The $1\varepsilon-2\varepsilon$ distance interferes with other distances of somewhat lower r -value so that no isolated peak will occur exactly at $r = 4.3$ Å. In the difference curves, however, the influence of the neighbouring distances should to a certain extent be subtracted and the peak at 4.3 Å should show up. In Fig. 3 the difference curves are given for the region mentioned. The $\frac{\sigma(r)}{r}$ curve for each of the four isomers β , γ , δ and ε has been subtracted from that of the α isomer. All these difference curves have maxima at 4.3 Å corresponding to the assumption that the α isomer has the form $\varepsilon\varepsilon\kappa\kappa$. The relatively small value of the height of the peak corresponding to the difference $\alpha - \beta$ is explained by assuming the β isomer to be of the form V (Table 1) characterized by the equilibrium $\varepsilon\kappa\kappa\varepsilon \rightleftharpoons \kappa\varepsilon\varepsilon\kappa$. The relatively large height of the peak for the difference $\alpha - \delta$ is easily explained by the fact that the $\frac{\sigma(r)}{r}$ curve of the δ isomer itself has a pronounced minimum at 4.3 Å introduced by neighbouring distances.

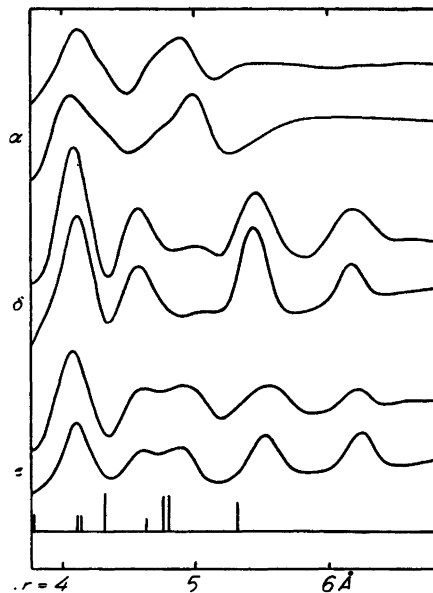


Fig. 4. Experimental and theoretical $\frac{\sigma(r)}{r}$ curves for the outer parts of α , δ and ϵ BTC.

To provide further evidence concerning the structure of the β isomer and to determine the structure of the γ and ϵ isomers the relative values for the areas and heights of pronounced peaks of the $\frac{\sigma(r)}{r}$ curves of the different isomers were studied. First of all the areas below the peak at about 4.12 Å were compared. The results are listed in Table 2. In the second column of the table the observed areas for the five isomers are given in an arbitrary unit. In the third column the calculated values for the various possibilities are listed in a sequence so that the correspondence with the values in the second column is as good

Table 2. Experimental and theoretical relative values for the areas under the peak at $r = 4.12$ Å for the various isomers.

Isomers	Experimental values	Theoretical values	Structure forms
α	5.0	5	$\epsilon \epsilon \kappa \kappa$
β	5.7	$6 \rightleftharpoons 4$	$\epsilon \kappa \kappa \epsilon \rightleftharpoons \kappa \epsilon \epsilon \kappa$
γ	6.7	7	$\epsilon \kappa \kappa \kappa$
δ	11.8	8	$\kappa \kappa \kappa \kappa$
ϵ	6.3	6	$\kappa \epsilon \kappa \kappa$

as possible. In the fourth column the corresponding structure forms are given. The present consideration seems to indicate that the structures of the two isomers γ and ϵ are characterized by the forms $\epsilon \kappa \kappa \kappa$ and $\kappa \epsilon \kappa \kappa$ respec-

tively. It further indicates that the β isomer probably has the structure $\varepsilon \kappa \kappa \varepsilon \rightleftharpoons \kappa \varepsilon \varepsilon \kappa$ the former being the predominating form.

Similar studies were carried through for the peak at r equal to 4.90 Å, and the results are listed in Table 3. The areas below this maximum are much influenced by neighbouring maxima as can be easily seen in Fig. 2. We have therefore found it more correct in this case to measure the heights of the peaks instead of the areas. The value 2 + for the $\varepsilon \varepsilon \kappa \kappa$ form and 1 + for

Table 3. Experimental and theoretical relative values of the heights of the peak at $r = 4.90$ Å for the various isomers.

Isomers	Experimental values	Theoretical values	Structure forms
α	2.4	2 +	$\varepsilon \varepsilon \kappa \kappa$
β	2.0	$2 \rightleftharpoons 2$	$\varepsilon \kappa \kappa \varepsilon \rightleftharpoons \kappa \varepsilon \varepsilon \kappa$
γ	1.6	1 +	$\varepsilon \kappa \kappa \kappa$
δ	—	0	$\kappa \kappa \kappa \kappa$
ε	1.3	1	$\kappa \varepsilon \kappa \kappa$

the $\varepsilon \kappa \kappa \kappa$ form mean that the calculated heights are somewhat greater than 2 and 1 respectively. An exact value can not be given unless information concerning the deviation from the ideal structures is obtained. The conclusions drawn from Table 3 support the ideas already given concerning the structure of the five isomers.

In the preceding discussion ideal structures as described in an earlier work³ were tacitly applied. The fine structures of the molecules were of less importance for these discussion though some of the discrepancies between observed and calculated values in Tables 2 and 3 must be ascribed to the deviations from the ideal structures. To make a comparison of experimental and calculated $\frac{\sigma(r)}{r}$ curves possible, deformations from the ideal structures must be taken into account. In Fig. 4 experimental and theoretical pairs of curves are given for the isomers α , δ and ε . Only the outer parts of the curves are reproduced. The theoretical curves are calculated by assuming the forms already found and by introducing deformations of the same kind and magnitude as those known for corresponding cyclohexane derivatives^{7,8}. The correspondence between experimental and calculated curves adds further evidence to our ideas of the structure of the three isomers α , δ and ε . Below the $\frac{\sigma(r)}{r}$ curve of the ε isomer the line diagram for the "conversion form" $\varepsilon \kappa \varepsilon \varepsilon$ not yet excluded is given. The line diagram can not be brought to agreement with the

$\frac{\sigma(r)}{r}$ curve of the ϵ isomer or that of any of the other isomers. This form may therefore be excluded.

The similarities of the $\frac{\sigma(r)}{r}$ curves for the β and γ isomers are so great that calculation of theoretical curves should not be expected to elucidate much further the structures of these two isomers. The only obvious difference in the general appearance is related to the shape of the shoulder at approximately 4.8 Å. This point is indeed in accordance with what should be expected from the structures already ascribed to these two isomers.

The above arguments concerning the structure of the α , δ and ϵ BTC can be regarded as conclusive. Concerning the β and γ isomers the electron diffraction work alone might leave some doubt, though strong arguments are in favour of the structures given. Fortunately the dipole moment measurements, on the other hand, must be regarded as quite conclusive for these two isomers³.

The structure forms containing more than two ϵ bonds were all excluded. Of course it is not possible from the electron diffraction studies alone to exclude the possibility of minor contribution of these forms to the equilibria indicated in Table 1. It should, however, be obvious from the above arguments that these less stable forms are not contributing to any great extent.

Finally it can be mentioned that the result of this work as well as the result of the dipole moment measurements³ is in agreement with the view expressed by the Ethyl Corporation team².

SUMMARY

The configuration of the five isomers of benzene tetrachloride α , β , γ , δ and ϵ have been studied by the aid of the electron diffraction sector method. The five isomers were attributed to the following forms: α ($\epsilon \epsilon \kappa \kappa$), β ($\epsilon \kappa \kappa \epsilon \rightleftharpoons \kappa \epsilon \epsilon \kappa$), γ ($\epsilon \kappa \kappa \kappa$), δ ($\kappa \kappa \kappa \kappa$) and ϵ ($\kappa \epsilon \kappa \kappa$).

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