

Deviation from Coplanarity of the Atoms in Structures of Halogen Substituted Benzenes

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The discovery of the quantum mechanical phenomenon of resonance has greatly contributed to the progress in the theory of the chemical bond. The theory has been able to explain well established experimental facts in cases where the older theories failed. On the other hand applications to effects, the existence of which may still be questioned, may bring discredit to the theory. It seems therefore most important to increase our experimental knowledge as far as possible before minor details in molecular structures are discussed using the resonance theory.

In aromatic compounds the resonance phenomena are very strikingly demonstrated. In benzene, for instance, the properties of the equivalent C-C-bonds is explained by assuming that they have 50 % single bond and 50 % double bond character. The C-C-distance in benzene is about 1.40 Å, *i. e.* it has a value between that usually observed for single bonds (1.54 Å) and that observed for double bonds (about 1.34 Å). According to a well-known theory resonance may also exist between double and single bonds in cases where the proportion of single and double bond character differs from that of benzene. If the percentage of double bond character exceeds 50 % the C-C-distance is smaller than 1.40 Å, if the percentage is less than 50 % the distance is greater.

Brockway and Palmer¹ have investigated the structures of some chlorine derivatives of benzene. The ortho Cl-Cl-distance was found to be greater than expected for an undistorted model. The effect was explained partly by assuming a small amount of double bond character of the C-Cl-bonds, resulting in a reduction of the double bond character of the bond between the two adjacent carbon atoms, partly by the assumption that the angle between the C-Cl-bonds is greater than 60°, both bonds remaining in the plane of the carbon ring.

In the hope of being able to contribute to the elucidation of this very interesting problem, we have applied the rotating sector method to it and obtained results which differ somewhat from those obtained by Brockway and Palmer. We think it worth while to give our results in some detail, not only because of the discrepancy just hinted at, but also because the examples treated seem well fitted for a comparison between the visual method and the sector method of electron diffraction.

A survey of the sector method in use for some years in this laboratory has recently been given in this journal ². Each of the $\frac{\sigma(r)}{r}$ -curves reproduced in present publication was obtained by Fourier synthesis of a mean molecular scattering curve which was the average of a series of scattering curves, each of which was computed from a separate diagram.

The following compounds were studied:

o-dichlorobenzene, *o*-dibromobenzene, hexachlorobenzene, hexabromobenzene, 1,2,3,5-tetrabromobenzene and *p*-dibromobenzene.

The C-C-bond distance gives rise to pronounced maxima in the $\frac{\sigma(r)}{r}$ -curves (at $r = 1.40\text{--}1.405 \text{ \AA}$) in all cases except in C_6Cl_6 and *p*- $\text{C}_6\text{H}_4\text{Br}_2$, where it is disturbed by the influence of higher neighbouring maxima. The C-Br-bond distance is found to be 1.88 \AA :

1.89(*o*- $\text{C}_6\text{H}_4\text{Br}_2$), 1.87 (C_6Br_6), 1.88 (1,2,3,5- $\text{C}_6\text{H}_2\text{Br}_4$ and *p*- $\text{C}_6\text{H}_4\text{Br}_2$).

The corresponding C—Cl-distance is found equal to 1.72 \AA (C_6Cl_6) and 1.735 ($\text{C}_6\text{H}_4\text{Cl}_2$). In each case the C-C and C-halogen bond distance found in the actual molecule will be used as the basis for calculating the dimensions of the models which we are going to discuss. In the two cases where the C-C bond distance was not directly observed, the value 1.40 \AA is used. With the exception of *p*- $\text{C}_6\text{H}_4\text{Br}_2$, all the models representing plane molecules give sets of interatomic distances which are in poor agreement with the values obtained from the $\frac{\sigma(r)}{r}$ -curves. The agreement in the case of the plane *p*- $\text{C}_6\text{H}_4\text{Br}_2$ molecule, however, is very satisfactory. We have calculated the interatomic distances in the other compounds, considering models in which C-halogen bonds are bent out of the plane of the C_6 -hexagon, and under these circumstances a much better correspondence between calculated and experimental distances is reached.

In the Figs. 1—6 the experimental $\frac{\sigma(r)}{r}$ -curves of the six compounds with

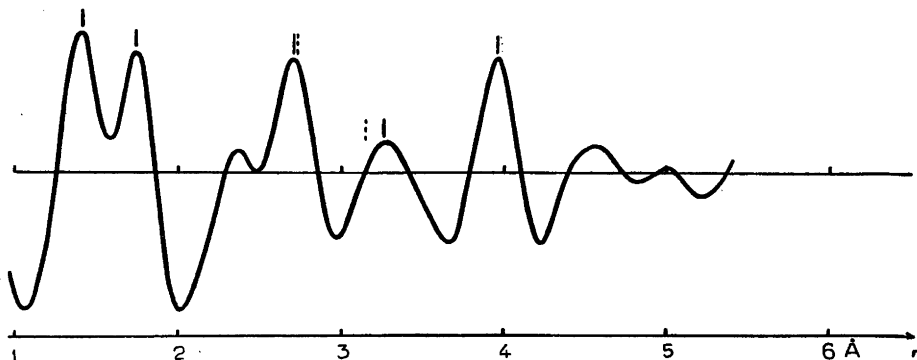


Fig. 1. $\frac{(\sigma r)}{r}$ -curve for *o*-dichlorobenzene.

which we are dealing are reproduced. In all these figures the r -values of distances occurring in the models under discussion are indicated by vertical lines, the broken lines corresponding to plane models, the fully drawn lines to models where halogen atoms are outside the plane of the carbon atoms. The Tables 1—6 contain values of the main distances, both experimental and theoretical, of the different molecules. Only such distances as may be determined with some accuracy from the $\frac{\sigma(r)}{r}$ -curves, have been tabulated. In the following discussion each compound will be treated separately.

o-Dichlorobenzene. (Fig. 1 and Table 1.) The experimental distances tabulated in the second column of the table are obtained directly from the $\frac{\sigma(r)}{r}$ -curve. The C_1-C_2 and the C_1-Cl_1 -distances are found to be 1.405 Å and 1.735 Å respectively. In the third column of the table theoretical values of the distances occurring in the plane model are tabulated. The fourth column contains theoretical values for a non-planar model in which the two C—Cl-bonds are bent 18° out of the C_6 -plane, perpendicular to this plane and in opposite directions. Both the table and figure show that the non-planar model gives a better agreement between experiment and calculation than the plane one.

Table 1. *o*- $C_6H_4Cl_2$. $C_1-C_2 = 1.405$ Å. $C_1-Cl_1 = 1.735$ Å.

| Distance | Experimental | Theoretical, plane | Theoretical, 18° |
|-------------|--------------|--------------------|------------------|
| C_1-Cl_2 | 2.70 Å | 2.72 Å | 2.70 Å |
| C_1-Cl_3 | 3.97 » | 4.03 » | 3.98 » |
| Cl_1-Cl_2 | 3.28 » | 3.14 » | 3.26 » |

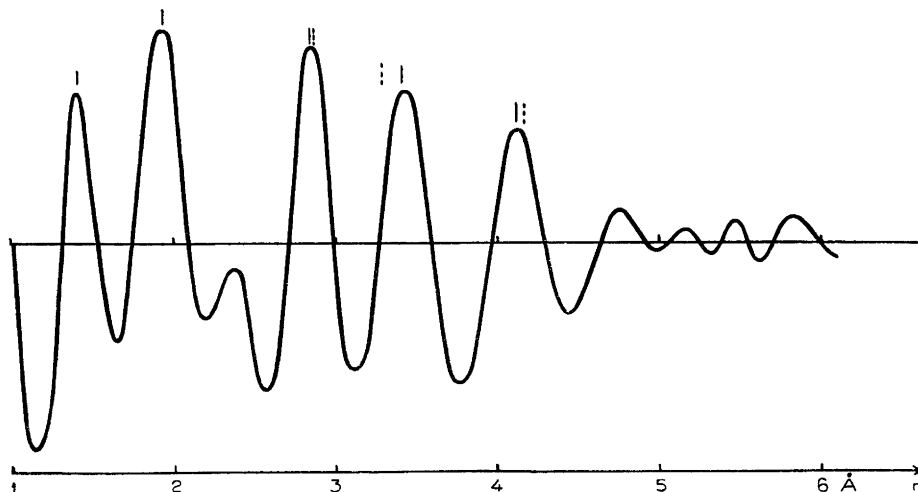


Fig. 2. $\frac{\sigma(r)}{r}$ -curve for *o*-dibromobenzene.

o-Dibromobenzene. (Fig. 2, Table 2.) The observed C_1-C_2 -distance is 1.405 Å, the C_1-Br_1 -distance 1.89 Å. From the figure and the table the same conclusion may be drawn as in the case of the corresponding chlorine compound. A bending of the C-halogen bonds like that described for the chlorine compound, and of the same magnitude, leads to the best agreement between calculation and experiment.

Table 2. $o-C_6H_4Br_2$. $C_1-C_2 = 1.405$ Å. $C_1-Br_1 = 1.89$ Å.

| Distance | Experimental | Theoretical, plane | Theoretical, 18° |
|-------------|--------------|--------------------|------------------|
| C_1-Br_2 | 2.85 Å | 2.86 Å | 2.84 Å |
| C_1-Br_3 | 4.13 » | 4.18 » | 4.13 » |
| Br_1-Br_2 | 3.43 » | 3.30 » | 3.42 » |

Hexachlorobenzene (Fig. 3, Table 3). The carbon-carbon bond distance is observed in the $\frac{\sigma(r)}{r}$ -curve, but the presence of the C—Cl-bond distance makes the condition for an accurate determination unfavourable. We have therefore used the value 1.40 Å found in other benzene derivatives as a basis for the calculation of the dimensions of the models. The value 1.72 Å was observed for the C—Cl-bond distance. A bending of the C—Cl-bonds out of the plane of the carbon hexagon is observed in this case as well, but the angle seems to

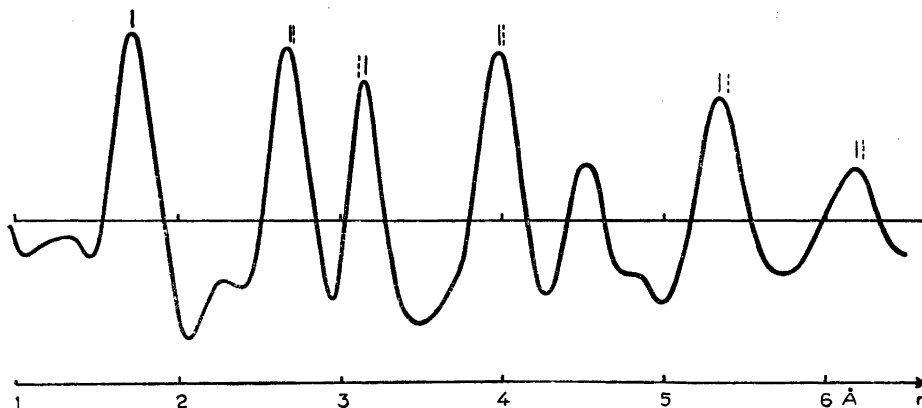


Fig. 3. $\frac{\sigma(r)}{r}$ -curve for hexachlorobenzene.

be somewhat smaller (about 12° instead of 18°) than in the two compounds mentioned above. Here, also, the figure and the table may best demonstrate the effect.

Table 3. C_6Cl_6 . $C_1-C_2 = 1.40 \text{ \AA}$. $C_1-Cl_1 = 1.72 \text{ \AA}$.

| Distance | Experimental | Theoretical, plane | Theoretical, 12° |
|-------------|-------------------|--------------------|-------------------------|
| C_1-Cl_2 | 2.68 \AA | 2.71 \AA | 2.70 \AA |
| C_1-Cl_3 | 3.99 » | 4.01 » | 3.99 » |
| C_1-Cl_4 | 4.51 » | 4.52 » | 4.50 » |
| Cl_1-Cl_2 | 3.15 » | 3.12 » | 3.16 » |
| Cl_1-Cl_3 | 5.35 » | 5.40 » | 5.34 » |
| Cl_1-Cl_4 | 6.19 » | 6.24 » | 6.20 » |

Hexabromobenzene (Fig. 4, Table 4). The carbon-carbon bond distance is found equal to 1.40 \AA , the C—Br-bond distance to 1.87 \AA . Here, also, the observed distances are best explained by assuming a bending of the C—Br-bonds of about 12° out of the plane of the benzene ring.

Table 4. C_6Br_6 . $C_1-C_2 = 1.40 \text{ \AA}$. $C_1-Br_1 = 1.87 \text{ \AA}$.

| Distance | Experimental | Theoretical, plane | Theoretical, 12° |
|-------------|-------------------|--------------------|-------------------------|
| C_1-Br_2 | 2.81 \AA | 2.84 \AA | 2.83 \AA |
| C_1-Br_3 | 4.12 » | 4.15 » | 4.13 » |
| C_1-Br_4 | 4.64 » | 4.67 » | 4.64 » |
| Br_1-Br_2 | 3.30 » | 3.27 » | 3.33 » |
| Br_1-Br_3 | 5.62 » | 5.66 » | 5.61 » |
| Br_1-Br_4 | 6.50 » | 6.54 » | 6.50 » |

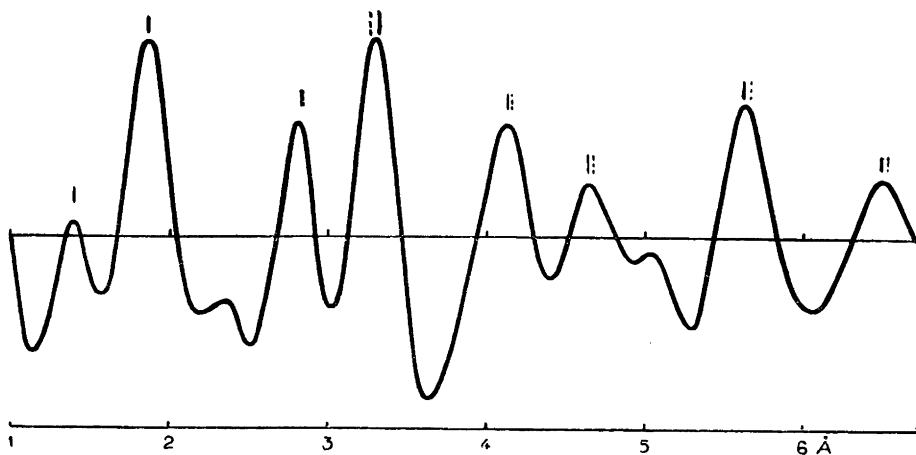


Fig. 4. $\frac{\sigma(r)}{r}$ -curve for hexabromobenzene.

1,2,3,5-Tetrabromobenzene (Fig. 5, Table 5). The C—C and C—Br-bond distances obtained are 1.40 Å and 1.88 Å respectively. There seems to be no reason for the assumption that the C₅—Br₅-bond is bent out of the ring plane. The assumption that the other C—Br-bonds are bent about 15° out of this

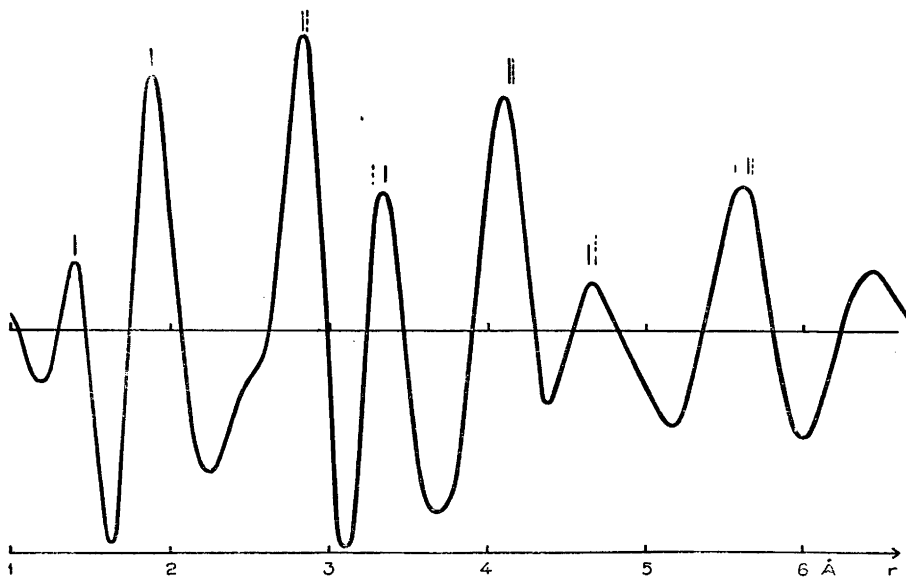


Fig. 5. $\frac{\sigma(r)}{r}$ -curve for 1,2,3,5-tetrabromobenzene.

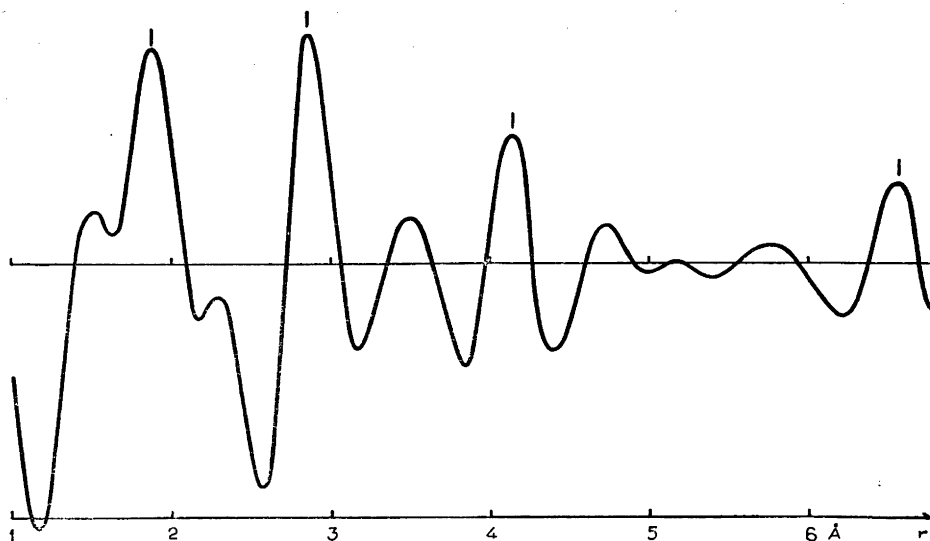


Fig. 6. $\frac{\sigma(r)}{r}$ -curve for *p*-dibromobenzene.

plane gives the best agreement between theory and experiment. It follows from this assumption (see Table 5 and Fig. 5) that the C_1-Br_3 , C_1-Br_4 and Br_1-Br_3 -distances are each split up into two components, lying some hundredths of an Ångström apart.

Table 5. $1,2,3,5-C_6H_2Br_4$. $C_1-C_2 = 1.40$ Å. $C_1-Br_1 = 1.88$ Å.

| Distance | Experimental | Theoretical, plane | Theoretical, 15° |
|-------------|--------------|--------------------|-----------------------------------|
| C_1-Br_2 | 2.83 Å | 2.85 Å | 2.83 Å |
| C_1-Br_3 | 4.11 » | 4.16 » | 4.13 Å; 4.16 Å (rel. weights 3:1) |
| C_1-Br_4 | 4.66 » | 4.68 » | 4.64 »; 4.68 » (rel. weights 3:1) |
| Br_1-Br_2 | 3.34 » | 3.28 » | 3.36 Å |
| Br_1-Br_3 | 5.62 » | 5.68 » | 5.57 »; 5.65 » (rel. weights 1:2) |

p-Dibromobenzene (Fig. 6, Table 6). This compound was investigated in order to check our assumption that the repulsion between *o*-substituted halogen atoms is responsible for the bending of the C-halogen bonds. From table and figure it is obvious that the distances observed are those to be expected for a plane model and that no disturbing effects can be observed.

Table 6. $p-C_6H_4Br_2$. $C_1-C_2 = 1.40$ Å. $C_1-Br_1 = 1.88$ Å.

| Distance | Experimental | Theoretical, plane |
|-------------|--------------|--------------------|
| C_1-Br_2 | 2.85 Å | 2.85 Å |
| C_1-Br_3 | 4.15 » | 4.16 » |
| Br_1-Br_4 | 6.56 » | 6.56 » |

DISCUSSION OF THE RESULTS

From the results of our experiments we have not been able to confirm the presence of systematic variation of the C—C-bond length. Discussing the accuracy of our measurements it should be born in mind that the determination of relative values of distances within the same molecule are more reliable than absolute values of such distances. This follows from the fact that our devices for precision measurements of the voltage (owing to post-war conditions) are not quite satisfactory. The greater differences in C—C and C-halogen distances do not, however, exceed 0.005 Å (C—C), 0.015 Å (C—Cl) and 0.02 Å (C—Br).

The reason for a deviation of the angle between two neighbouring C-halogen bonds from the value of 60° is no doubt chiefly a result of repulsive forces between halogen atoms. The distances to be expected in absence of such deviation are 3.13 Å (Cl—Cl) and 3.28 Å (Br—Br); both values which must be assumed to be smaller than the double van der Waals' radii, which should be at least 3.3 Å and 3.5 Å respectively.

It is striking that the deviation seems to be greater in the case of 1,2-halogen derivatives than in the hexa-compounds. It should be remembered, however, that the entire discussion was based upon the assumption that the bending of the C-halogen bonds takes place in planes normal to the benzene ring. Actually, this must be true in the hexa-derivatives, but in less symmetric molecules, like the *o*-dihalogenbenzenes, the bending will of course have two components, one perpendicular to the benzene ring and one in the plane of the ring. The latter component will influence the distance of 1,2-halogen atoms much more strongly than other distances. The result is that it becomes rather more difficult to determine the magnitude of this »planar effect» than that of the other. In the case of 1,2,3,5-tetrabromobenzene the bending of the C₂—Br₂-bond must be orthogonal to the benzene ring, the C₅—Br₅-bond remaining in the ring plane. The distortion process just mentioned is able to explain the fact that the bending angle, if the bending is assumed to take place perpendicularly to the benzene ring only, is found to be smaller in the C₆X₆ molecules than in the others. It seems very likely that the perpendicular component of bending is in reality very much the same in all cases, and that an additional »planar effect» occurs in less symmetrical molecules.

It is clear that the *o*-dihalogenbenzenes, if not plane, may exist in two optically active forms, but the conversion from the one form to the other must be expected to take place rather frequently so that a separation of the two antipodes will be impossible. It seems very unlikely, however, that this may be treated as an oscillation and that the intermediate forms may contribute

noticeably to the scattering of electrons. Similar considerations should be expected to be applicable to the conversion of the symmetrical molecules where mirror-image forms are identical.

The so-called «ortho-effect» of dipole moments can of course at least partly be explained by the increase in angle between the ortho C—X-bonds. Thus the determined dipole moment of 1,2,4-trichlorobenzene is 1.25 D, whereas the moment of the undisturbed molecule should be equal to that of the mono-derivative (1.56 D), and the calculated value, if the C₁—Cl₁ and C₂—Cl₂-bonds are bent 18° perpendiculary to the benzene ring, would be 1.45 D. If a bending *in* the plane is also accounted for, the calculated value will be still less than 1.45. In the case of 1,2,3,5-chlorobenzene and the corresponding bromo-compound, the low value of 0.7 D would also be better accounted for if a bending in the benzene ring takes place besides the perpendicular distortion. The fact that induction phenomena will always tend to diminish the dipole moments makes conclusions of this kind rather questionable, however.

The results obtained by us differ markedly from those obtained by Brockway and Palmer who used the visual method. A comparison between the potentialities of the two methods seems therefore justified. We consider it most convenient to choose a special example, and in Fig. 7 we reproduce some theoretical intensity curves (A—F), taken from Brockway and Palmer's paper (Fig. 4, p. 2185), corresponding to a set of slightly different models of the o-dichlorobenzene molecule. The vertical lines give the position of the maxima and minima visually observed from the diffraction diagrams. According to the authors mentioned it is possible to decide which of these alternative models gives the best approximation to the true molecule simply by comparing the position of the maxima and minima with the experimental positions indicated by the vertical lines.

Below the curves A—F we have given an experimental molecular scattering curve using the same *s*-scale. The general agreement between our experimental curve and the calculated curves is striking. In fact, the positions of the maxima and minima of the theoretical curves are generally in better accordance with those of our experimental curve than with the positions of the maxima and minima visually observed. In spite of this, and of the fact that the whole intensity curve is known and based on photometrically measured intensities, it occurs to us that it would be unjustified, for example, to state that the curve D is better than E.

The question now arises, why the Fourier-transformed curve, $\frac{\sigma(r)}{r}$, may be better suited than the molecular scattering curve for the purpose of picking out the best molecular model. The $\frac{\sigma(r)}{r}$ -curve of course expresses the same ex-

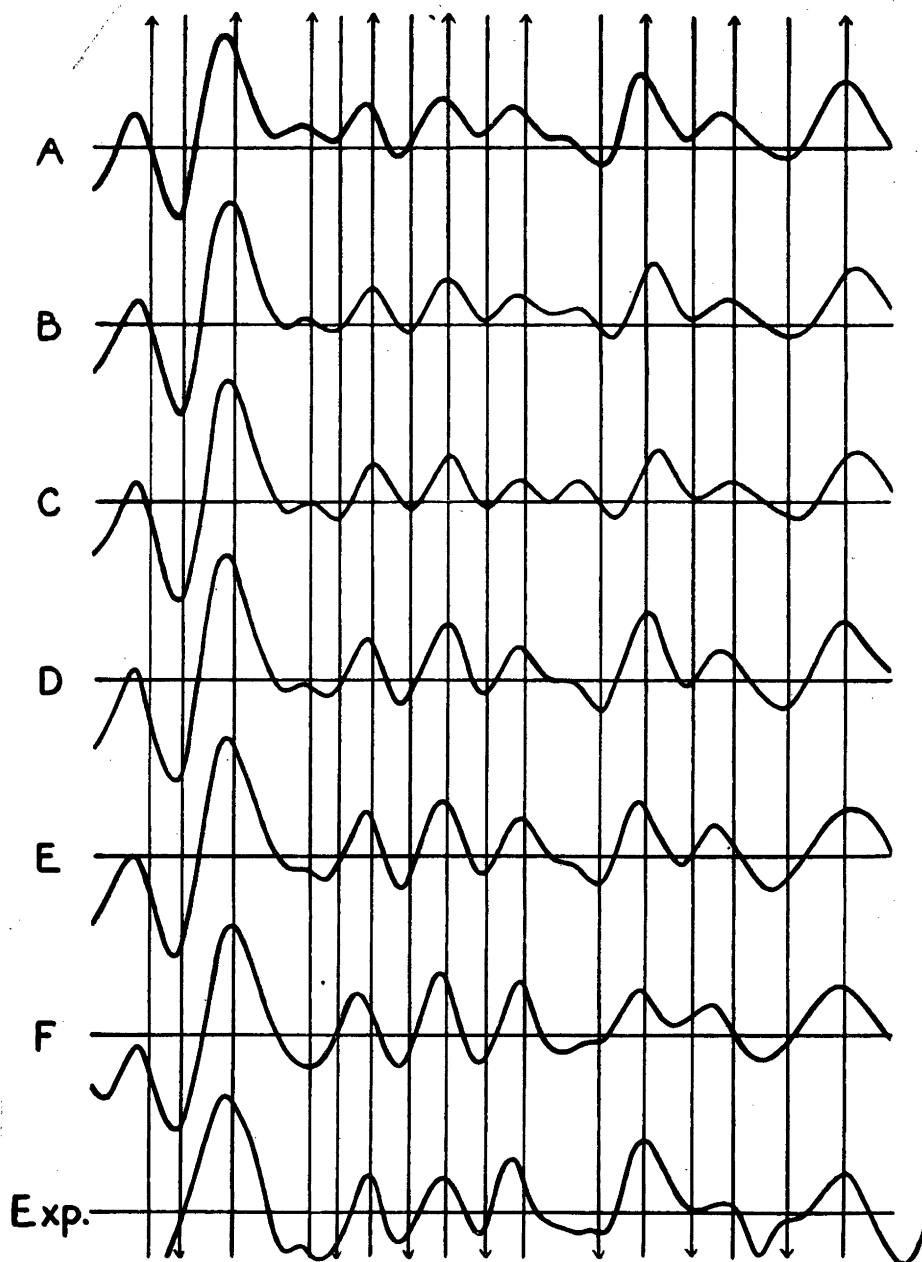


Fig. 7. A...F theoretical intensity curves for *o*-dichlorobenzene according to Brockway and Palmer. Exp. experimental curve obtained by the sector method.

perimental facts as the molecular scattering curve. Nevertheless, the $\frac{\sigma(r)}{r}$ curve has the advantage of concentrating the effect of a certain internuclear distance within a rather short range, usually giving rise to pronounced maxima, whereas the corresponding contribution of the intensity curve is sinusoidal and thus distributed over the whole curve. On the other hand a certain error in the experimental intensity curve will usually be distributed over the entire $\frac{\sigma(r)}{r}$ curve and therefore not lead to serious consequences. Should the error happen to be sinusoidal, however, and range over a greater part of the intensity curve, it will have a noticeable effect on the curve. But an error of this type is in general very improbable.

SUMMARY

The following compounds have been investigated using the electron diffraction method with rotating sector: *o*-C₆H₄Cl₂, *o*-C₆H₄Br₂, C₆Cl₆, C₆Br₆, 1,2,3,5-C₆H₂Br₄ and *p*-C₆H₄Br₂. The results are compared with those obtained by Brockway and Palmer¹.

The effects reported by these authors could not be confirmed. Our observations are in favour of non-planar models for these molecules, the single exception being the *p*-dibromobenzene. The forces acting between *o*-halogen atoms tend in general to bring the halogen atoms out of the plane of the benzene ring. Finally a comparison between the visual method and the rotating sector method has been carried out.

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