

Electron Diffraction Investigations of Molecular Structures

II. Results Obtained by the Rotating Sector Method

O. HASSEL and H. VIERVOLL*

Universitetets Kjemiske Institutt, Blindern — Oslo, Norway

An extensive work on the structure of gaseous molecules was carried out in this laboratory during the period 1940—46, using the electron diffraction method designated as the »sector method». From photometer records of the diffraction diagrams scattering curves were obtained, and distribution functions were then computed using Fourier analysis. A survey of the methods developed for this purpose is given in a separate paper¹. This paper is intended to give a corresponding survey of the more important results of structure determinations carried out during the period just mentioned. The difficult conditions, especially regarding facilities of publication, have so far prevented us from publishing our results in periodicals easily available outside Scandinavia. References to the original papers will be given throughout the following survey.

The paper is divided into three parts. The first part deals with the structure of simple compounds, chosen in order to get experience regarding the new methods before more complicated problems were tackled. In the second part results of the molecular structure determinations of some halogen derivatives of ethane are given. The third part of our survey has been reserved for structure determinations of molecules containing isocyclic or heterocyclic rings.

It should be emphasized that the structure of a number of the molecules in question is so complicated that a determination was possible only on the basis of a comprehensive study of simpler compounds and the use of differential methods described in some detail in the preceding survey.

* We wish to express our sincere gratitude towards *Fridtjof Nansens Fond* and *Statens Forskningsfond* for economical aid without which this work could not have been accomplished.

In order to save space, reproductions of intensity curves are not given here. An example of a photometric record of a sector diagram (benzene) is reproduced in fig. 4 of the preceding paper.

I. THE STRUCTURE OF SOME SIMPLE MOLECULES

Br_2 and I_2 .² The experimental distribution function $\sigma_m(r)$ for a diatomic molecule is given in fig. 6 of the preceding paper. From the distribution curves the internuclear distances are easily obtained. Iodine and bromine were investigated and the following distances obtained: Br-Br = 2.28 Å. I-I = 2.67 Å.

CO_2 and CS_2 .² The distribution curves indicate two internuclear distances with a ratio of 1 : 2 corresponding to a symmetrical, rectilinear molecule. The atomic distances obtained were: C-O = 1.15 Å. C-S = 1.56 Å.

AsI_3 .² The distribution curve reveals two internuclear distances only: As-I = 2.54 Å, I-I = 3.85 Å. The molecule is pyramidal and symmetrical with an angle I-As-I = 98.5°.

CCl_4 and CBr_4 .³ The experimental distribution curves, $\sigma_m(r)$ and $\sigma(r)$ for CBr_4 are given in fig. 7 of the preceding paper¹. Both for CCl_4 and CBr_4 the distribution curves indicate only the two internuclear distances to be expected for regular tetrahedrons. The atomic distances are found to be C-Cl = 1.76 Å and C-Br = 1.94 Å.

CH_3I and CH_2I_2 .⁴ Because of the small scattering power of hydrogen, the $\frac{\sigma(r)}{r}$ curves, fig. 1, give only the two distances C-I and I-I. For both substances the C-I distance is found equal to 2.12 Å. The I-I distances are found to be 3.535 Å in CH_3I and 3.569 Å in CH_2I_2 . This correspond to an angle I-C-I of 113.0° in iodoform and 114.7° in methylene iodide.

C_2Cl_2 .⁵ The structure of dichloro-acetylene derived by de Laszlo⁶ from electron diffraction diagrams could easily be shown to be incorrect. The $\sigma_m(r)$ curve is shown in fig. 2. The maxima of this curve correspond to the r values 1.20 Å, 1.64 Å, 2.83 Å and 4.425 Å. The molecule must therefore be linear and symmetrical and correspond to the formula Cl-C \equiv C-Cl, the atomic distances being C-C = 1.195 Å, C-Cl = 1.64 Å.

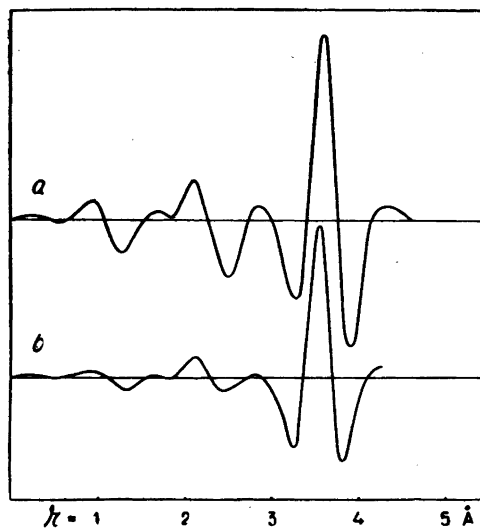


Fig. 1. Experimental $\frac{\sigma(r)}{r}$ curves of iodine (a) and methylene iodide (b).

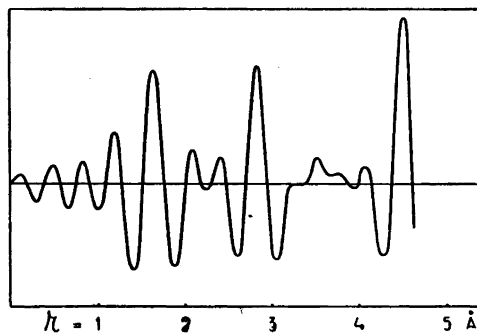


Fig. 2. Experimental $\sigma_m(r)$ curve of C_2Cl_2 .

P_4S_3 . The $\sigma_m(r)$ function of this substance — reproduced in fig. 3 exhibits two pronounced maxima at 2.15 Å and 3.48 Å, the origin of the other maxima may be explained on the assumption that they are the consequences of diffraction effects¹. The most probable structure will be that of fig. 4 in which all the bond distances are about 2.15 Å and the distances between atoms not directly linked to each other about 3.48 Å. In order to demonstrate the relationship between the P_4S_3 and the P_4 structures, a model of the P_4 molecule is included in fig. 4. It is seen that the introduction of one S atom between

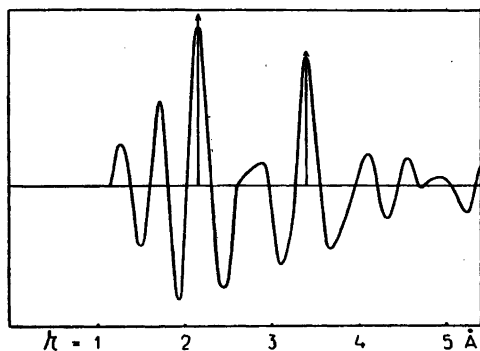


Fig. 3. Experimental $\sigma_m(r)$ curve of P_4S_3 .

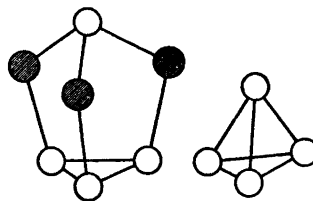


Fig. 4. Models of the P_4S_3 and P_4 molecules.

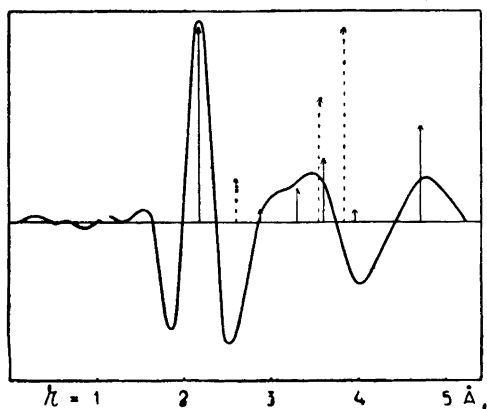
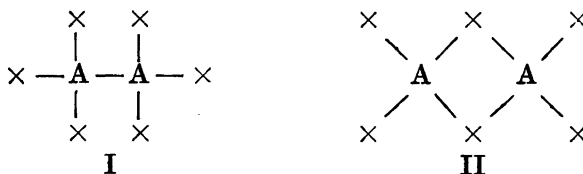


Fig. 5. Experimental $\sigma(r)$ curve of Fe_2Cl_6 .

one of the phosphorous atoms of P_4 and each of the three other P atoms transforms the P_4 molecule into a P_4S_3 molecule. The valency angles in P_4S_3 are all about 100° except those of the P_3 triangle. The near structural relationship existing between P_4S_3 and P_4 makes the conformity in chemical properties appear reasonable. A very striking example is the behaviour of the two substances towards gaseous oxygen.

Fe_2Cl_6 .⁸ In the case of molecules A_2X_6 two possible structures have been proposed, the ethane-like structure I and the ethylene-like structure II:



The $\sigma(r)$ curve of gaseous Fe_2Cl_6 has one pronounced maximum only (fig. 5) and the r -value of this maximum — 2.17 \AA — must no doubt correspond to the shortest Fe-Cl distance of the molecule. The dotted arrows of fig. 5 give the atomic distances of the ethane-like structure and the fully drawn arrows give the distances of the ethylene-like structure of the molecule. It is evident that only the ethylene-like structure is in agreement with the experimental $\sigma(r)$ curve.

The results of an investigation dealing with the aluminium halides Al_2Cl_6 , Al_2Br_6 and Al_2I_6 has not been conclusive, chiefly because of the relatively poor scattering power of the Al atoms.

II. THE STRUCTURE OF SOME HALOGEN SUBSTITUTED ETHANES

The structure of ethane and its simple derivatives is of considerable interest because their elucidation will contribute to the knowledge about the forces between atoms not directly linked together and the nature of the rotation about C-C single bonds.

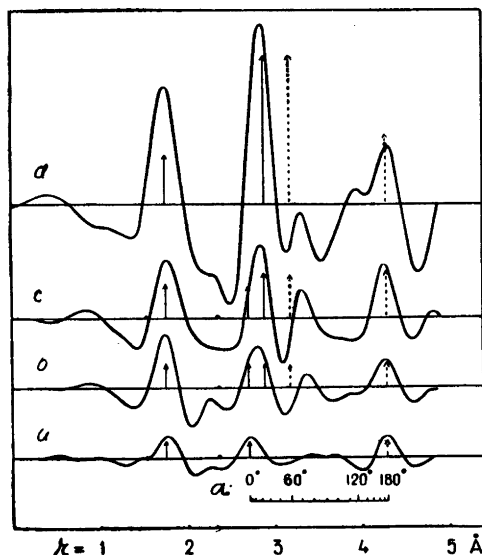


Fig. 6. Experimental $\sigma(r)$ curves of $\text{CH}_2\text{Cl} \cdot \text{CH}_2\text{Cl}$ (a); $\text{CHCl}_2 \cdot \text{CH}_2\text{Cl}$ (b); $\text{CHCl}_2 \cdot \text{CH}_2\text{Cl}$ (c) and $\text{CCl}_3 \cdot \text{CCl}_3$ (d).

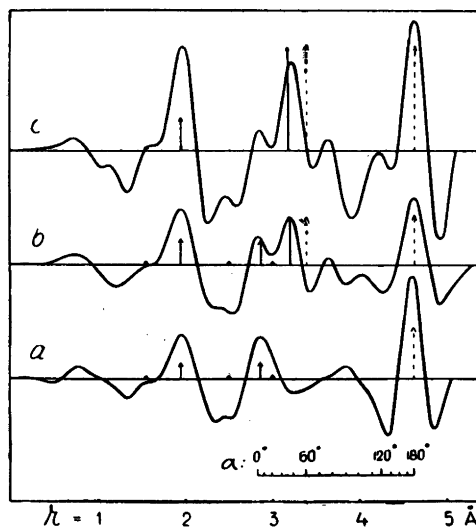


Fig. 7. Experimental $\sigma(r)$ curves of $\text{CH}_2\text{Br} \cdot \text{CH}_2\text{Br}$ (a); $\text{CHBr}_2 \cdot \text{CH}_2\text{Br}$ (b) and $\text{CHBr}_2 \cdot \text{CHBr}_2$ (c).

The results published by different authors and based on dipole moment measurements, spectroscopical studies and electron diffraction analysis using the «visual» method have led to diverging interpretations. In tackling the question by the new methods of electron diffraction we chose the chlorine and bromine derivatives because of the relatively great scattering power of the halogens. The $\sigma(r)$ curves of the following seven compounds were worked out and discussed in detail⁹:

*1,2 dichloro-ethane; 1,2 dibromo-ethane;
1,1,2 trichloro-ethane; 1,2,3 tribromo-ethane;
1,1,2,2 tetrachloro-ethane; 1,1,2,2 tetrabromo-ethane;
hexachloro-ethane.*

The $\sigma(r)$ curves are reproduced in figs. 6 and 7. The resemblance between curves of corresponding chlorine and bromine compounds is striking. The existing differences are those to be expected because of the greater scattering power of the bromine atom. The C-C distance is 1.54 Å, the smallest C-Cl distance in all the chlorine compounds (fig. 6) is 1.76 Å and the corresponding C-Br distance (fig. 7) is 1.94 Å. In both figures the r values of atomic distances which should be constant and independent of an intramolecular rotation about

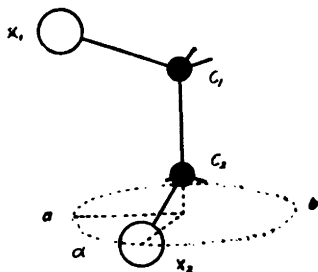


Fig. 8. Relative position of two halogen atoms bonded to different carbon atoms. At (a) $\alpha = 0^\circ$ (cis position) and at (b) $\alpha = 180^\circ$ (trans position).

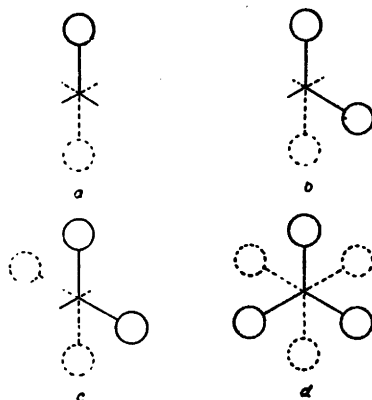


Fig. 9. Trans models of halogen substituted ethanes. (a) $\text{CH}_3\text{X}-\text{CH}_2\text{X}$; (b) $\text{CHX}_2-\text{CH}_2\text{X}$; (c) $\text{CHX}_2-\text{CHX}_2$; (d) CX_3-CX_3 .

the carbon-carbon bond are indicated by fully drawn arrows, the length of the arrows being proportional to the theoretical $\sigma(r)$ values. There is no evidence for a distortion of the tetrahedral valency angles.

The distance between two halogen atoms X_1 and X_2 of which X_1 is directly linked to the carbon atom C_1 and X_2 to C_2 will be influenced by a rotation about the C_1-C_2 bond. The relative position of the halogen atoms is most conveniently described by giving the angle α between the two planes $\text{X}_1\text{C}_1\text{C}_2$ and $\text{X}_2\text{C}_2\text{C}_1$ (fig. 8). The possible values of this angle range from $\alpha = 0^\circ$ to $\alpha = 180^\circ$. In the «cis» position ($\alpha = 0^\circ$) the X_1-X_2 distance has its minimum value, and attains its greatest possible value in the «trans» position ($\alpha = 180^\circ$). The scales at the bottom of figs. 6 and 7 are intended to illustrate in which way the X_1-X_2 distances depend on the angle α . As a matter of fact all the experimental curves exhibit sharp maxima corresponding to trans positions of two halogen atoms ($\alpha = 180^\circ$). The mutual position of the two tetrahedral groups in the trans models of the different molecules is given by fully drawn and dotted lines in fig. 9. The dotted arrows in figs. 6 and 7 indicate the atomic distances in these models which depend on the relative position of the two groups. The r values corresponding to $\alpha = 180^\circ$ are in good agreement with the experimental curves. No maxima appear, however, for distances corresponding to $\alpha = 60^\circ$. These discrepancies are removed if we interpret the models of fig. 9 as representing the position of equilibrium of the different molecules and assume an oscillation of the two tetrahedral groups to take place about this position. Such an oscillation will alter the distance

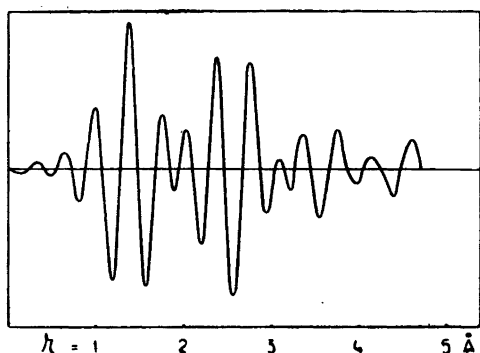


Fig. 10. Experimental $\sigma_m(r)$ curve of benzene.

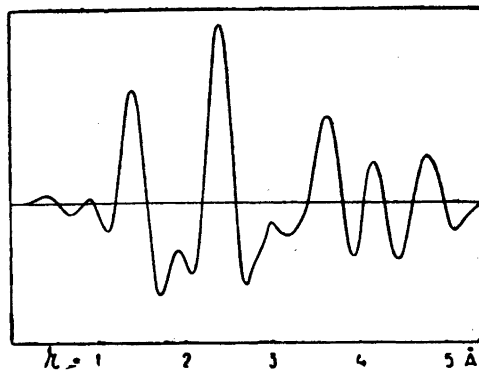


Fig. 11. Experimental $\sigma(r)$ curve of phloroglucinol.

between atoms in trans position very little. In the chlorine and bromine compounds which we are considering, a variation of α from 180° to 170° will cause a decrease of the halogen-halogen distance smaller than 0.01 \AA . Distances corresponding to $\alpha = 60^\circ$, however, will be much more sensitive to a change in α , a decrease or increase of 10° producing a decrease or increase of the distance of about 0.15 \AA . In accordance with this, the maxima corresponding to $\alpha = 180^\circ$ are always very pronounced and the r values only a little smaller than those calculated for the true trans position. Maxima corresponding to $\alpha = 60^\circ$, however, are flattened out and cannot be observed because of the influence of other maxima and their diffraction effects. Although no accurate information concerning the amplitude of oscillation is given, the small displacement of the trans maxima indicates a mean value of about $15\text{--}20^\circ$.

The distances between hydrogen and halogen atoms, one of which is linked to C_1 , the other to C_2 , is 2.88 \AA (Cl) and 3.10 \AA (Br). As pointed out¹⁰ these distances agree very well with the sums of van der Waals radii of a hydrogen atom and a halogen atom. This relation seems to be confirmed by the investigations of cyclohexane derivatives which will be discussed below.

III. THE STRUCTURE OF SOME CYCLIC COMPOUNDS

*Benzene*¹. The experimental $\sigma_m(r)$ curve of benzene vapour is given in fig. 10. The curve is in complete agreement with the planar, hexagonal structure. The shortest C-C distance is equal to 1.40 \AA , the C-H bond distance to 1.04 \AA .

*Fluorobenzene*² was also investigated using the sector method. The results concerning the benzene ring were confirmed. The observation indicate that

the fluorine atom is situated on the line drawn between two para C atoms, the C-F distance being 1.31 Å.

*Phloroglucinol*¹². The $\sigma(r)$ curve, reproduced in fig. 11, give conclusive evidence for the fact that the C- and O-atoms are coplanar and the internuclear distances correspond to those which would be expected for 1,3,5 trioxybenzene. This distances given by the curve are C-C = 1.40 Å, C-O = 1.36 Å. The corresponding distances to be expected for 1,3,5 cyclohexanetrion are C-C = 1.54 Å; C-O = 1.16 Å. A calculation of the energy shows that the enol structure must be considerably more stable than the keto structure, so that only a very small fraction of the latter should be present in the equilibrium mixture. The results of Kohlrausch¹³ concerning the C-X bond energies in aliphatic and aromatic compounds are in good agreement with this result.

*Cyclopropane*¹⁴. The $\frac{\sigma(r)}{r}$ curve of this compound is very simple, as may be seen from fig. 12. It is obvious that the second of the three maxima observed at $r = 1.08$ Å, $r = 1.54$ Å and $r = 2.24$ Å gives the C-C distance in the three-membered ring and the other maxima the two C-H distances occurring in a symmetrical molecule. From these distances the valency angles C-C-H and H-C-H are found to be 116.4° and 118.2° respectively.

*Cyclopentane*¹⁵. The experimental $\frac{\sigma(r)}{r}$ curve is given in the upper part of fig. 13 and is seen to have a maximum for $r = 1.54$ Å, the C-C bond distance. If the ring is planar and symmetrical the second C-C-distance will have the value 2.49 Å. It is easily seen, however, that a C-H distance must occur which will tend to displace the maximum due to this C-C distance. In order to obtain the value of this C-H distance a special sort of subtraction process was performed. A theoretical $\frac{\sigma(r)}{r}$ curve including the diffraction effects was computed for the C-C distances of the regular pentagon. At the bottom of the figure the curve representing the difference between the experimental curve and this theoretical curve is given. This curve would be expected to exhibit maxima for r values equal to the three C-H distances of the symmetrical molecule. The first maximum of the curve occurs for $r = 1.09$ Å. If the C-H distance has this value and the H-C-H angle of the methylene groups has its normal tetrahedral value, the second and third C-H distances should be 2.17 Å and 3.22 Å. The r values of the corresponding maxima of the differential curve are 2.18 Å and 3.13 Å. The last maximum is broad and little

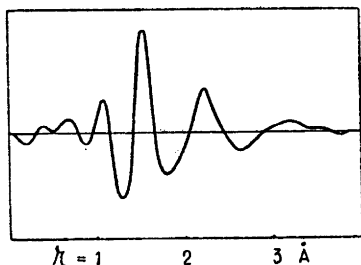


Fig. 12. Experimental $\frac{\sigma(r)}{r}$ curve of cyclopropane.

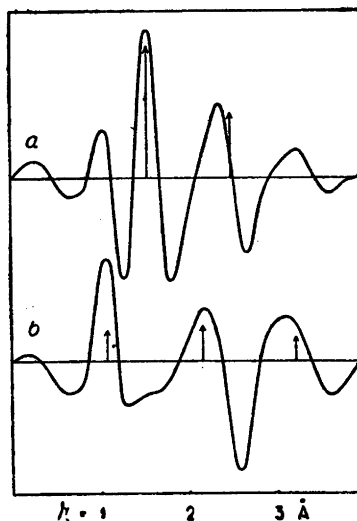


Fig. 13. (a) Experimental $\frac{\sigma(r)}{r}$ curve of cyclopentane. (b) Difference between the curve (a) and the theoretical curve for the carbon skeleton.

pronounced. The conclusion seems justified that a deviation from a symmetrical pentagonal structure with H-C-H angles of about 109.5° if it exists, must be very limited.

Cyclohexane. Earlier investigations based on the visual method¹⁶ agreed with the staggered form of the molecule (fig. 14) in which all valency angles are assumed to be $109^\circ 28'$. Results from our laboratory, some of which have been published¹⁷, confirm this conclusion.

It is found that the model, when based upon a C-C bond distance of 1.54 Å and a C-H distance of 1.10 Å, gives atomic distances which are in satisfactory agreement with the experimental $\sigma(r)$ curve (fig. 15). In no case has an examination of the structure of cyclohexane or its derivatives so far given reliable indications of the presence of a less symmetrical form of the carbon skeleton. The reason seems to be that other possible forms would make distances between atoms linked to different carbon atoms of the ring smaller than the sum of their van der Waals radii⁹.

The bonds between the carbon atoms of the symmetrical cyclohexane ring and other atoms are of two geometrically different kinds. Bonds of one kind are parallel to the trigonal axis of the ring. These »upright» bonds

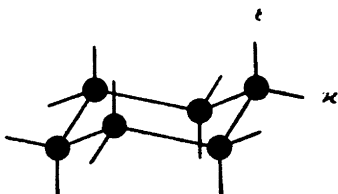


Fig. 14. The staggered form of the cyclohexane molecule. κ - and ε -bonds are indicated.

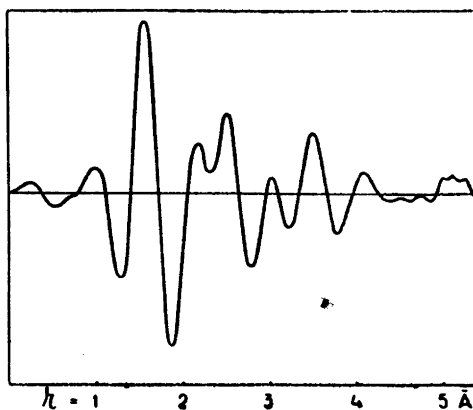


Fig. 15. The experimental $\sigma(r)$ curve of cyclohexane.

(*ἑστρηκῶς*) have been designated as ε -bonds. Bonds of the second kind are roughly orthogonal to the principal axis (the angle being $109^{\circ}28'$ instead of 90°) and have been called κ -bonds (*κειμενῶς*, prostrate). Now, without breaking the carbon-carbon bonds, a conversion of the ring may take place into a new ring of the same shape in which, however, each ε -bond is a κ -bond of the old ring and vice versa. The significance of the distinction between κ - and ε -bonds will, we hope, be brought out clearly in the following part of our paper where the configurations of molecules containing six-membered rings are discussed.

*Chloro-cyclohexane*¹⁸. In a single mono-derivative of cyclohexane, like chloro-cyclohexane, there are two possible configurations, the ε -form and the κ -form. The only atomic distances which are different in the two forms and contribute some weight to the electron scattering of the molecule are the distances from the chlorine atoms to the carbon atoms. The fully drawn curve in the upper part of fig. 16 is the experimental $\sigma(r)$ curve of chloro-cyclohexane. It is difficult indeed to draw any conclusion regarding the structure of the chlorine compound directly from this curve. An examination of the curve, reproduced in the lower part of fig. 16 and representing the difference between the experimental $\sigma(r)$ curves of the chloroderivative and that of cyclohexane (fig. 15) is able, however, to give better informations concerning the position of the chlorine atom. The maxima of this curve should correspond to r values giving the C-Cl distances of the molecule. Arrows at the bottom of fig. 16 indicate the calculated r values in the ε - and κ -form respectively. The

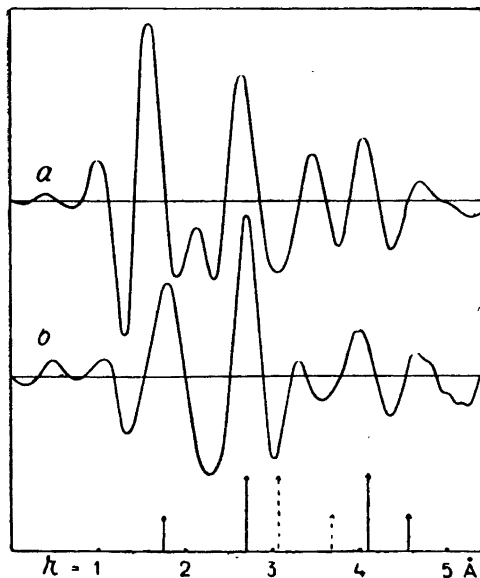


Fig. 16. (a) The experimental $\sigma(r)$ curve of chloro-cyclohexane. (b) The difference between the experimental $\sigma(r)$ curves of chloro-cyclohexane and cyclohexane.

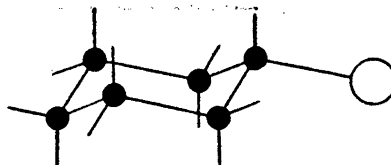


Fig. 17. Model of the chloro-cyclohexane (and cyclohexylmercaptane) molecule (κ -form).

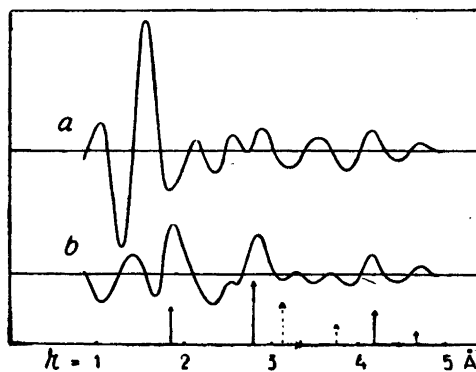


Fig. 18. (a) The experimental $\frac{\sigma(r)}{r}$ curve of cyclohexylmercaptane. (b) The difference between the experimental $\frac{\sigma(r)}{r}$ curves of cyclohexylmercaptane and cyclohexane.

two first arrows to the left indicate C-Cl distances common to both models whereas the two remaining fully drawn arrows correspond to distances characteristic of the κ -form given in fig. 17. The two dotted arrows indicate C-Cl distances present in the ϵ -form only. The calculations are based on the bond distances C-Cl = 1.76 Å and C-C = 1.54 Å. The lengths of the arrows are proportional to the weights of the distances in question. It is seen that the curve does not give any indication of the presence of the ϵ -form, but the presence of the κ -form seems obvious. The conclusion must be drawn that the concentration of the κ -form is at least considerably greater than that of the ϵ -form.

The energy of the ϵ -form must therefore be greater than that of the κ -form, a fact which is not surprising. In a model of the ϵ -form the distance between the chlorine atom and the two nearest hydrogen atoms (both of which are ϵ -atoms) would be nearly equal to the distance between a chlorine and a hydrogen atom linked to different carbon atoms in «cis» forms of chlorinated

ethanes (p. 153). This distance of about 2.5 Å is no doubt smaller than the sum of the van der Waals radii of the two atoms. On the other hand, the distance between a κ -chlorine atom and the hydrogen atoms linked to neighbouring C atoms is nearly equal to the distance characteristic of the stable forms of chlorinated ethanes.

*Cyclohexylmercaptan*¹⁹. The discussion of the structure of this compound was based on the experimental $\frac{\sigma(r)}{r}$ curve reproduced in the upper part of fig. 18. The curve obtained by subtracting the experimental $\frac{\sigma(r)}{r}$ curve of cyclohexane from that of the mercaptan is given in the lower part of the figure. The arrows below this curve indicate the r values of C-S distances to be expected in the ϵ - and κ -forms of cyclohexylmercaptan where the C-S bond distance is assumed to be 1.87 Å. In complete analogy with the chlorine compound the two smallest distances would be the same in both models. Here also the two remaining, fully-drawn arrows indicate distances present only in the κ -form and the two dotted arrows the distances to be expected in the ϵ -form. The experiment thus gives clear indications of the presence of the κ -form but not the ϵ -form.

1,4 dioxan. A series of compounds containing six-membered rings of oxygen and sulphur atoms is of interest when stereochemical problems related to the structure of cyclohexane are discussed. The structures of 1,4 dioxan and 1,4 dithian were therefore worked out in our laboratory by Ore.

The most pronounced maxima of the experimental $\frac{\sigma(r)}{r}$ curve (fig. 19 a) of 1,4 dioxan correspond to the r values 1.44 and 2.33 Å. A determination of the structure is not possible, however, on the basis of this fact alone. A comparison of the experimental curve with theoretical curves including diffraction effects was therefore carried out for different molecular models. The procedure of calculation has been described in a previous paper¹. Neither a planar model or any model of cradle type was able to deliver a theoretical curve in satisfactory agreement with the experimental one. The only model fulfilling this requirement was the staggered form shown in fig. 20. So far the result obtained by Sutton and Brockway²⁰ using the visual method was thus confirmed. According to these authors the bond distances and valency angles have the following values: C-O = 1.46 Å, C-C = 1.51 Å, \angle C-C-O = 109.5°, \angle C-O-C = 110°.

The theoretical $\frac{\sigma(r)}{r}$ curve based on this model is given in fig. 19 (dotted

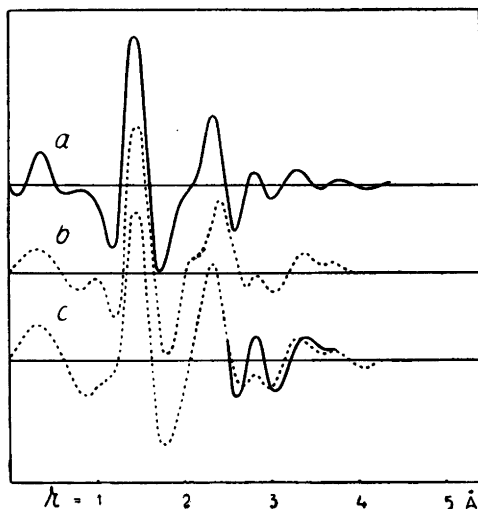


Fig. 19. (a) The experimental $\frac{\sigma(r)}{r}$ curve of dioxane. (b) Theoretical $\frac{\sigma(r)}{r}$ curve of Sutton and Brockways model. (c) Theoretical $\frac{\sigma(r)}{r}$ curve of the model given in this paper.

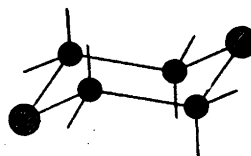


Fig. 20. Staggered form of the dioxane molecule.

curve b). A somewhat better agreement with our experimental curve was obtained when introducing slight modifications in the distances given by Sutton and Brockway. We found the best agreement to be reached when choosing C-C = 1.54 Å, C-O = 1.42 Å, \angle C-C-O = 106° and \angle C-O-C = 108°.

In calculating the theoretical curve corresponding to this model, the hydrogen atoms have also been taken into consideration. The C-H distance was assumed to be 1.10 Å and the H-C-H angle = 112°. The resulting curve is the dotted curve c of fig. 19. In this model there are four ϵ -hydrogen atoms, and the distance between two and two of them is only 2.16 Å. This distance is smaller than the double van der Waals radius of hydrogen — 2.5 Å — which nearly coincides with the distance in cyclohexane or the stable form of ethane¹⁰. We should expect, therefore, that the C-H bonds are not rigorously parallel but bent a certain angle out from the middle of the ring. In fact, the part of the theoretical $\frac{\sigma(r)}{r}$ curve lying in the region about $r = 2.8$ Å is in better agreement with the experimental curve if a bending of 10–12° is supposed to take place (*cf.* the fully drawn part of curve c in fig. 19). It is difficult to decide to which extent minor details like these can be relied on. They have

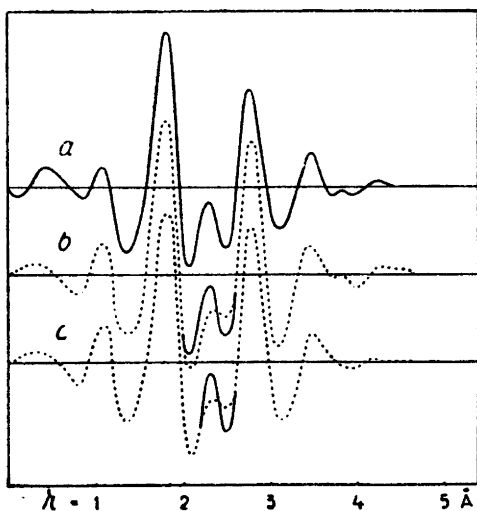


Fig. 21. (a) The experimental $\frac{\sigma(r)}{r}$ curve of dithian. (b) Theoretical $\frac{\sigma(r)}{r}$ curve of the staggered form of the molecule. (c) Theoretical $\frac{\sigma(r)}{r}$ curve of the model given in fig. 22.

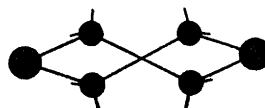


Fig. 22. Possible model of the dithian molecule.

been mentioned, however, because similar results were obtained also in the case of dithian.

1,4 dithian. The experimental $\frac{\sigma(r)}{r}$ curve is the fully drawn curve *a* of fig. 21. A comparison between this curve and a series of theoretical curves based on different molecular models led to the result that the staggered form of fig. 20 is the most probable in this case also. The atomic distances and the angles leading to the most satisfactory agreement with the experimental curve are: S-C = 1.81 Å, C-C = 1.54 Å, \angle S-C-C = 111° and \angle C-S-C = 100°.

The theoretical $\frac{\sigma(r)}{r}$ curve for this model is the dotted curve *b* of fig. 21. In addition to the distances and angles given above, the distance C-H was assumed to be 1.10 Å, and the angle S-C-H 109.5°. Here again, however, as in the case of dioxane, the theoretical $\sigma(r)$ curve is in better agreement with the experimental curve if the S-C-H angle is assumed to be smaller than 109.5°. The fully drawn part of curve *b*, fig. 21 which gives a better agreement in the region near 2.3 Å, is based on the angle S-C-H = 105°.

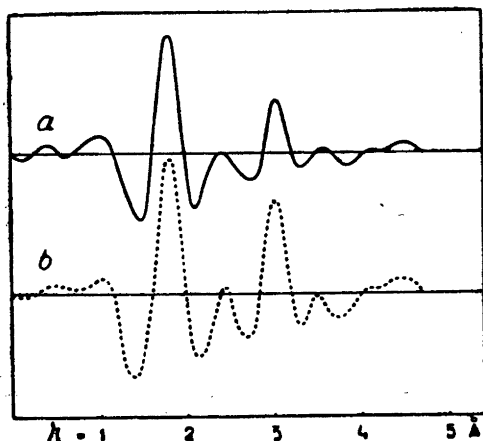


Fig. 23. (a) Experimental $\frac{\sigma(r)}{r}$ curve of trithian. (b) Theoretical $\frac{\sigma(r)}{r}$ curve of the staggered form fig. 24.

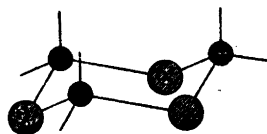


Fig. 24. Model of the trithian molecule.

Besides the staggered form of dithian, another model of the molecule has to be taken into consideration because it leads to a theoretical curve (dotted curve *c* of fig. 21) which agrees surprisingly well with the experimental curve. This model, given in fig. 22, is strainless and it may in fact be transformed into the «cradle» form without deformation of the valency angles. The model possesses two digonal axis of symmetry, the atomic distances and valency angles are C-S = 1.81 Å, C-C = 1.54 Å, \angle S-C-C = 109.5° and \angle C-S-C = 104.5°.

The remarkable conformity between the $\frac{\sigma(r)}{r}$ curve of dithian and the theoretical curve based on this model suggests that molecules of this form may be present in equilibrium with molecules of the staggered form. This seems probable because the energy difference between the two forms cannot be expected to be considerable.

Sym-trithian. This substance contains a symmetrical ring of alternate sulphur and carbon atoms and is of special interest because we are going to discuss the structures of α - and β -trithioacetaldehyde below. The experimental $\frac{\sigma(r)}{r}$ curve of trithian exhibits two pronounced maxima at $r = 1.81$ Å and $r = 3.05$ Å, as may be seen from the fully drawn curve *a* of fig. 23. The atomic distance S-C being 1.81 Å, the second maximum should correspond to the

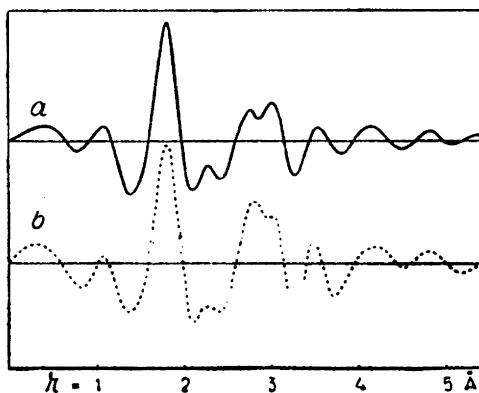


Fig. 25. (a) Experimental $\frac{\sigma(r)}{r}$ curve of α -trithioacetaldehyde. (b) Theoretical $\frac{\sigma(r)}{r}$ curve of the κ, κ, ϵ -model (fig. 27).

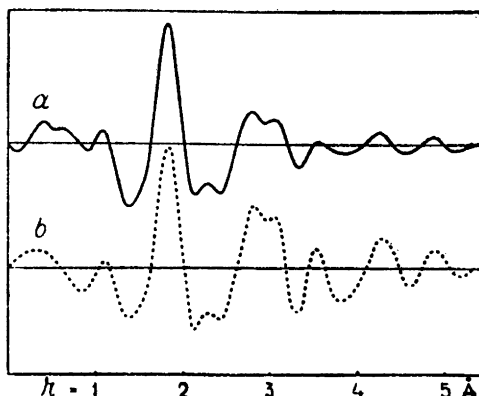


Fig. 26. (a) Experimental $\frac{\sigma(r)}{r}$ curve of β -trithioacetaldehyde. (b) Theoretical $\frac{\sigma(r)}{r}$ curve of the κ, κ, κ -model (fig. 28).

S-S distance. This leads to a C-S-C angle of 114.5° . The influence of other atomic distances on the $\frac{\sigma(r)}{r}$ curve is not great and consequently the determination of these distances is difficult. It seems reasonable to assume, however, that the ring will have very nearly the same form in trithian, α - and β -trithioacetaldehyde and, if that is so, the trithian molecule has the staggered form of fig. 24 with an angle S-C-S = 106.5° . Assuming the C-H distance to be 1.10 \AA the theoretical $\frac{\sigma(r)}{r}$ curve including diffraction effects (dotted curve *b* of fig. 23) is seen to be in very good agreement with the experimental curve.

α - and β -trithioacetaldehyde²¹. Baumann and Fromm²² and later Chattaway and Kellett²³ based their discussion of the configurations of these molecules on the assumption of a planar ring. The first-mentioned authors arrived at the conclusion that the α -compound (m. p 101° C) is the «cis» form and the β -compound (m. p $125\text{--}126^\circ \text{ C}$) the «trans» form. Chattaway and Kellett, on the other hand, discovered that the α -compound is able to give two different monosulphones but the β -compound only one, and consequently came to the opposite conclusion.

The results to which we were led in the case of trithioformaldehyde makes it seem improbable that the ring is planar in either of these substances. Electron diffraction investigations confirmed this view. The fully drawn curve

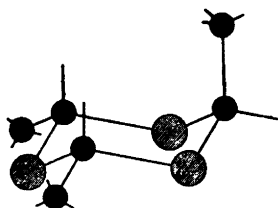


Fig. 27. Model of the α -trithioacetaldehyde molecule (κ,κ,ϵ -form).

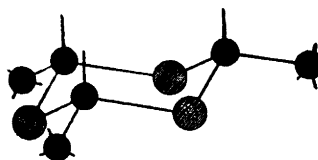


Fig. 28. Model of the β -thioacetaldehyde molecule (κ,κ,κ -form).

a of fig. 25 gives the experimental $\frac{\sigma(r)}{r}$ curve of the α -compound, the corresponding curve of fig. 26 that of the β -compound. The conformity of these experimental curves is very striking. The most pronounced maxima of both curves correspond to r values equal to 1.81 Å and 3.05 Å, the values observed also in the case of trithioformaldehyde. These indicate that the C_3S_3 ring must be very similar for all three substances. A comparison between the experimental $\frac{\sigma(r)}{r}$ curves and theoretical curves shows that a ring based on the distances C-S = 1.81 Å, the angle C-S-C = 106.5° and the angle S-C-S = 114.5° leads to a very satisfactory agreement in all cases.

The circumstance that the S-C-S angle is greater than 109.5° makes it very probable that the angle between the two other carbon valencies is somewhat smaller than the tetrahedral angle. The ϵ -valencies are not far from perpendicular to the C_3 and S_3 triangles, the angle they form with the normal of these plans being 2—3° only. It is evident that the properties of the two sorts of bonds (ϵ - and κ -bonds) already discussed in the case of cyclohexane derivatives will be of importance for trithioacetaldehyde as well. Thus steric hindrance will tend to prevent molecules having more than one ϵ -methylgroup from being formed, but the two configurations κ,κ,ϵ and κ,κ,κ should both be possible. The first of these forms is shown in fig. 27 the second in fig. 28.

Theoretical $\frac{\sigma(r)}{r}$ curves were computed for both forms choosing a C-C distance of 1.54 Å and a S-C-C angle of 106°. The curve corresponding to the configuration κ,κ,ϵ is the dotted curve of fig. 25. The dotted curve of fig. 26 corresponds to the κ,κ,κ form. The agreement between experimental and theoretical curves is so marked that very little doubt can remain as to the correctness of our models. It is obvious that the changes produced in the $\frac{\sigma(r)}{r}$ curve when one ϵ -methyl group in the κ,κ,κ form is replaced by an ϵ -group is relatively unimportant. So in order to decide which of the two

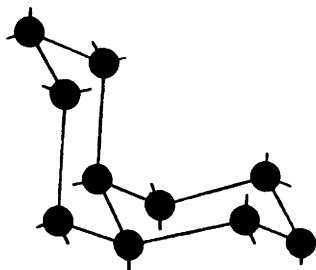
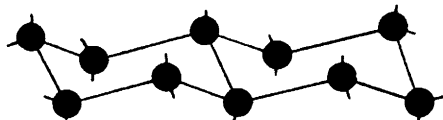


Fig. 29. Model of the »trans» decalin molecule. Fig. 30. Model of the »cis» decalin molecule.

compounds has the κ, κ, κ configuration and which the $\kappa, \kappa, \varepsilon$ configuration the fact mentioned above, that the α -compound forms two monosulphones, the β -compound only one, has to be taken into consideration. The result is then unambiguous: the α -compound corresponds to the configuration $\kappa, \kappa, \varepsilon$ (fig. 27) the β -compound to κ, κ, κ (fig. 28).

*The decalins*²⁴. It was pointed out some years ago¹⁰ that the symmetrical model of decalin (fig. 29) containing two staggered cyclohexane rings will probably be the correct model of the »trans» isomer, but that the »cis» model proposed by Mohr²⁵ and containing two »cradle»-shaped rings has to be rejected and replaced by a model (fig. 30) based on two staggered cyclohexane rings. Of these models the former results if two cyclohexane ring are linked together in 1,2 position using two κ bonds, the latter if one κ bond and one ε bond is used. The proposed structure of the so-called »cis» decalin should be energetically more stable than the Mohr structure because of its more favourable hydrogen-hydrogen distances.

The upper curve *a* of fig. 31 is the experimental $\frac{\sigma(r)}{r}$ curve of »trans» decalin, the lower curve *b* that of »cis» decalin. The conformity of the two curves is very striking. Only in the region between 2 and 4 Å differences are observed. In order to test the correctness of the proposed structure of the »cis» compound the experimental $\frac{\sigma(r)}{r}$ curve of the »trans» compound was subtracted from the corresponding curve of the »cis» compound.

The resulting curve (fig. 32 *b*) was compared with theoretical curves calculated under the assumption that the »trans» decalin has the structure of fig. 29. Fig. 32 *a* gives this theoretical differential curve based on the »cis» model of fig. 30, and fig. 32 *c* gives the corresponding curve based on the Mohr »cis» model. A comparison between these curves seems to settle beyond doubt that »cis» decalin has the structure given in fig. 30.

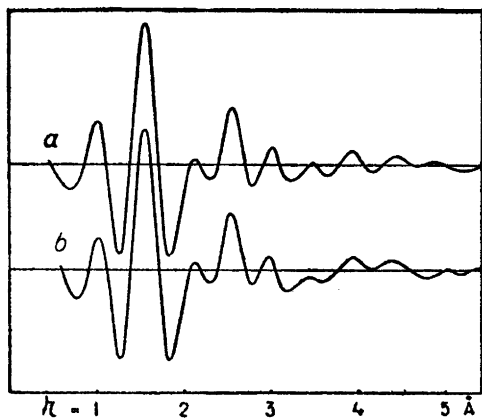


Fig. 31. (a) Experimental $\frac{\sigma(r)}{r}$ curve of «trans» decalin. (b) Experimental $\frac{\sigma(r)}{r}$ curve of «cis» decalin.

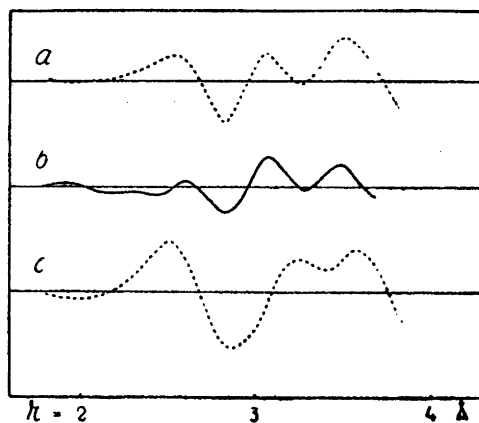


Fig. 32. (a) The difference between the theoretical $\frac{\sigma(r)}{r}$ curves of «trans» and «cis» decalin («cis» model fig. 30). (b) The difference between the experimental $\frac{\sigma(r)}{r}$ curves of «trans» and «cis» decalin. (c) The difference between the theoretical $\frac{\sigma(r)}{r}$ curves of «trans» and «cis» decalin («cis» model proposed by Mohr).

SUMMARY

Results of molecular structure determinations carried out in Oslo in the years 1940—46 by the rotating sector method of electron diffraction in vapours with subsequent Fourier analysis are given. The substances investigated include some simple organic compounds, halogen derivatives of ethane and finally a series of cyclic compounds. Among the latter substances containing six-membered rings identical with, or closely related to that of cyclohexane have been most extensively studied.

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