

## The Structure of 1,2-Epoxy-cyclohexane

### An Electron Diffraction Investigation Based on the Rotating Sector Method

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#### CHEMICAL PREPARATION

1,2-Epoxy-cyclohexane,  $C_6H_{10}O$ , was prepared according to the method of Brunel<sup>1</sup> by treating 2-iodo-cyclohexanol-(1),  $C_6H_{10}OH \cdot I$  with KOH in ether. The epoxide was purified by distillation.

#### ELECTRON DIFFRACTION-DIAGRAMS

A number of electron diffraction diagrams of 1,2-epoxy-cyclohexane were taken, using the rotating sector method. The microphotometer records of the different plates showed intensity curves in satisfactory agreement. The Fourier analysis was therefore based on a mean intensity curve. The evaluated  $\sigma(r)/r$  curve is shown in fig. 1 a. With regard to the theoretical deduction of the  $\sigma(r)/r$  function attention is drawn to a survey of the method developed at this institute. Reference to the original papers, published in the years 1940—46, will be found in this survey<sup>2</sup>.

#### DETERMINATION OF THE STRUCTURE OF THE EPOXIDE FROM THE $\sigma(r)/r$ CURVES

From chemical evidence we may draw the conclusion that the epoxide consists of one six-membered ring of C-atoms and one three-membered ring containing two C-atoms and one O-atom. These two rings have one edge in common. To simplify the discussion of the different models of the molecule, the C-atoms are given numbers from 1 to 6, as shown in fig. 2.

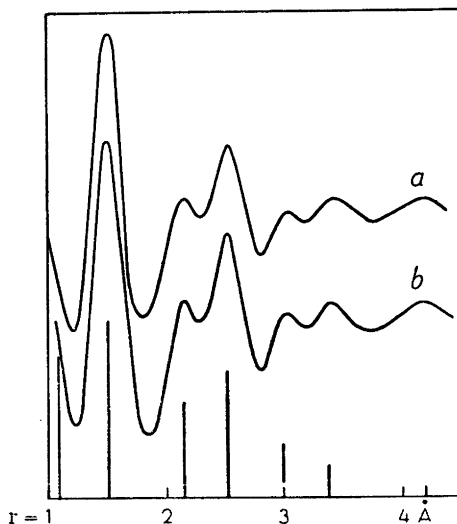


Fig. 1. a Experimental  $\sigma(r)/r$  curve. b Theoretical  $\sigma(r)/r$  curve. The vertical lines indicate height and  $r$ -value of the maxima of the seven normal curves, the sum of which is the theoretical  $\sigma(r)/r$  curve.

From a previous investigation of the molecular structure of cyclohexane<sup>3</sup>, we know that the cyclohexane ring has the »stair case» form, but an electron diffraction examination of  $C_6H_{12}$  does not give conclusive evidence as to whether or not small amounts of the »cradle»-shaped molecules are present. The repulsion between the H-atoms in this form, however, should render this form energetically unfavourable and under normal conditions the tilted ring is more likely than the »cradle»-shaped. All experimental facts seem to support this view. In general the H-atoms of two neighbouring  $CH_2$ -groups of a cyclic polymethylene will tend to occupy »trans» positions, similar to the stable form of ethane or the symmetrical form of the cyclohexane molecule. In three- or four-membered rings the »cis» positions cannot be avoided. In these cases the H-C-H-angle of the methylene group is not necessarily the tetrahedral angle ( $109.5^\circ$ ). In cyclopropane, for example, an angle of  $118.2 \pm 2^\circ$  is found<sup>4</sup>.

Starting with a normal cyclohexane ring, it is easy to see that the O-atom may be attached to two neighbouring C-atoms in different ways:

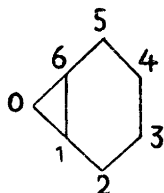


Fig. 2. Numeration of the atoms in 1,2-epoxy-cyclohexane.

1. We may engage two  $\kappa$ -bonds in the formation of the three-membered ring, bringing the two C-O-bonds into the same plane. This will necessarily result in a deformation of the six-membered ring, the C-C-C angles becoming smaller than the tetrahedral angle of the undeformed cyclohexane-ring. It is seen from fig. 3 a that the resulting model will be assymmetrical and should exist in two optically active forms, the one being the mirror image of the other. A transformation of one of these forms into the other or into any other form, cannot be performed without breaking chemical bonds.

2. By using one  $\kappa$ - and one  $\varepsilon$ -bond of the cyclohexane ring and bringing the two bonds into the same plane, two different situations may arise.

In the first place the tilted six-membered ring may be transformed into a »cradle»-shaped ring. The resulting model will be either that of fig. 3 b or that of fig. 3 c. The two models may be transposed with each other without breaking chemical bonds. If the stresses present in the three-membered ring cause deformations of the »cradle»-shaped six-membered ring, this will produce an increase of the C-C-C angles above the value  $109.5^\circ$ .

In the second place the choice of one  $\kappa$ - and one  $\varepsilon$ -bond may also lead to a deformed six-membered ring of the type shown in fig. 3 d. Here the atoms  $C_1, C_2, C_5, C_6$ , are coplanar and one of the atoms  $C_3$  and  $C_4$  is situated above and one below this plane. Of all the models this involves the least deformation of the »staircase»-shaped cyclohexane-ring.

3. Two  $\varepsilon$ -bonds point in opposite directions and any formation of an epoxide based on an  $\varepsilon, \varepsilon$ -model is impossible, unless the six-membered ring is transposed; thereby transforming all  $\varepsilon$ -bonds into  $\kappa$ -bonds.

In fig. 3 the four types of models are shown in projection. The double rings indicate two C-atoms placed one above the other.

In order to decide which model corresponds to the real structure of the epoxide, we may construct theoretical  $\sigma(r)/r$  curves for the different models and compare them with the experimental  $\sigma(r)/r$  curve.

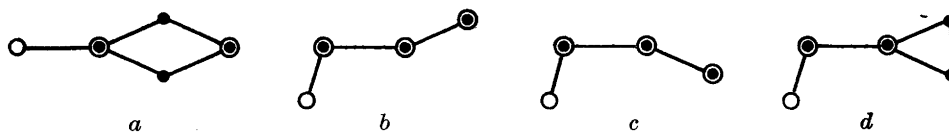


Fig. 3. Different types of models of the 1,2-epoxy-cyclohexane molecule shown in projection. The open ring indicates the O-atom. The double rings indicate two C-atoms, one placed above the other. Model a is produced by engaging two  $\kappa$ -bonds, and the others by engaging one  $\kappa$ -bond and one  $\varepsilon$ -bond in the formation of the three-membered ring.

These  $\sigma(r)/r$  curves may, however, be interpreted as the sum of two sets of normal curves<sup>7</sup>. The first set is derived from the distances between all C- and H-atoms, the second from the distances between the O-atom on the one hand and all the C- and H-atoms on the other. In all the proposed models the distances of the first set must lie within comparatively narrow limits. This is a consequence of the fact that the distance between neighbouring C-atoms is 1.54 Å and the valency angles in the six-membered ring does not differ very much from 109.5°. From this it is evident that it will be difficult to differentiate between the various models on the basis of the distances in the six-membered ring.

In order to attain any result we must use the distances of the second set, where the C-O-distances dominate. For each proposed model a  $\sigma(r)/r$  curve for the first set was constructed by correcting an experimental  $\sigma(r)/r$  curve for cyclohexane, by means of normal curves for the single distances. The resulting curve was subtracted from the experimental  $\sigma(r)/r$  curve for the epoxide. The difference curve represents the sum of the normal curves for the second set of distances. From this difference curve we can deduce the O-C-distances, and if we have chosen the correct model for the six-membered ring, these experimentally determined O-C-distances have to agree with the model.

$\sigma(r)/r$  curves for the first set of distances and corresponding difference curves were then constructed for models of all the proposed types (fig. 3), the models being deformed in varying degree. The O-C-distances which emerged were largely independent of the particular form of the six-membered ring. All reasonable models, that is to say those with a angle C-C-C- between 100° and 120°, give four different O-C-distances, all lying within the limits below:

$$\begin{array}{ll}
 \text{O}-\text{C}_1 = \text{O}-\text{C}_6 & = 1.42 \text{ \AA} \\
 \text{O}-\text{C}_2 = \text{O}-\text{C}_5 & = 2.49-2.53 \text{ \AA} \\
 \text{O}-\text{C}_3 & = 2.98-3.10 \text{ \AA} \\
 \text{O}-\text{C}_4 & = 3.25-3.40 \text{ \AA}
 \end{array}$$

This obliges us to reject model 3 a. The O-C-distances cannot agree with this model, unless all the C-C-C-angles are deformed so as to make the six C<sub>1</sub>-C<sub>3</sub>-distances approximately 1.9 Å. Such a short C<sub>1</sub>-C<sub>3</sub>-distance is very improbable, and moreover the experimental  $\sigma(r)/r$  curve plainly shows that this distance is very nearly 2.50 Å. In addition to this, the model cannot give different O-C<sub>3</sub> and O-C<sub>4</sub> distances.

Further investigations prove that the models 3 b and 3 c may be adjusted to agree with the O-C-distances, if all the C-C-C-angles are deformed to approximately 118° and the two forms exist in equilibrium. So large a deformation

of all the angles seems improbable, however, it is certainly reasonable to assume that the angles  $C_1-C_6-C_5$  and  $C_6-C_1-C_2$  are about  $118^\circ$ . In cyclopropane <sup>4</sup> the corresponding angle is found to be  $116.4 \pm 2^\circ$ . A simple quantum mechanical calculation of the effect produced on the valency angles at the C-atom, when one of the valency angles is decreased, supports this assumption <sup>5</sup>.

It should be pointed out however that a deformation of the other four C-C-C-angles in the six-membered ring to approximately  $118^\circ$ , is energetically improbable. On the contrary there is every reason to believe that these angles lie much closer to the value of the tetrahedral angle. Assuming the angles  $C_1-C_6-C_5$  and  $C_6-C_1-C_2$  to be approximately  $118^\circ$ , then models of the type, shown in fig. 3 d, are produced by building up the rest of the six-membered ring, leaving the other C-C-C-angles as close to the tetrahedral value ( $109.5^\circ$ ) as possible. We may presume that particularly the angles  $C_3-C_4-C_5$  and  $C_2-C_3-C_4$  deviate little from the tetrahedral value. Models of this type will also cause as many as possible of the H-atoms connected to neighbouring C-atoms to come into trans position. When testing different models of this type, the angles  $C_3-C_4-C_5$  and  $C_2-C_3-C_4$  were assumed to be tetrahedral. Different values for the angles  $C_6-C_1-C_2$  and  $C_1-C_6-C_5$  were then systematically tried. The last two angles are determined, when the six-membered ring is assumed to have a symmetry axis through the middle points of the  $C_1-C_6$  and  $C_3-C_4$  bonds.

In fig. 4 theoretical  $\sigma(r)/r$  curves for the second set of distances (the O-C- and O-H-distances) are shown together with the corresponding difference curves derived by subtracting the theoretical  $\sigma(r)/r$  curve for the first set of distances from the experimental  $\sigma(r)/r$  curve for the epoxide. A model of type 3 d with the angle  $C_6-C_1-C_2 = C_1-C_6-C_5 = 118.5^\circ$  apparently gives the best agreement between the two corresponding curves.

From fig. 3 d it is easily seen that the model may correspond to two optically active isomers. These can be transposed with each other without any chemical bond being broken, and it will scarcely be possible to separate them. But this transposition of the six-membered ring may also involve the occurrence of models of the type 3 b and 3 c as unstable forms during the transposition.

#### CONSTRUCTION OF THE THEORETICAL $\sigma(r)/r$ CURVE FOR THE EPOXIDE

If we now try to build up a theoretical  $\sigma(r)/r$  curve for the epoxide corresponding to the model of type 3 d with an angle  $C_1-C_6-C_5 = 118.5^\circ$ , this may be done in a simple way by putting all the interatomic distances of any significance in the model into seven groups. Then the difference between the distances within each group will not be more than 0.15 Å. We may now build up the

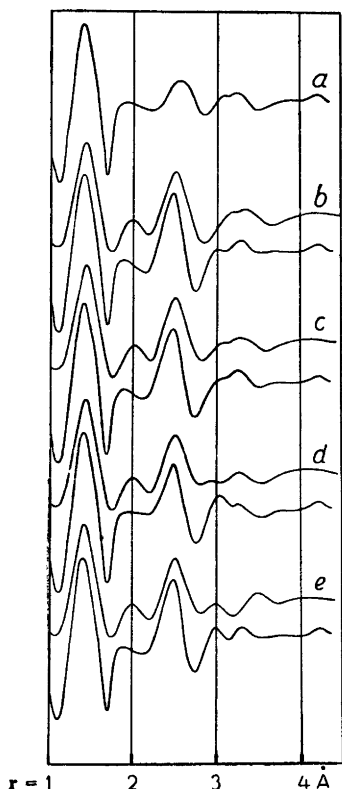


Fig. 4. Theoretical  $\sigma(r)/r$  curves for the second set of distances (the O-C- and O-H-distances) shown together with the corresponding difference  $\sigma(r)/r$  curves: a Difference between experimental  $\sigma(r)/r$  curves of 1,2-epoxy-cyclohexane and cyclohexane. b Theoretical  $\sigma(r)/r$  curve and below this the corresponding experimental difference  $\sigma(r)/r$  curve for the model of the epoxide molecule shown in fig. 3 d with the angle  $C_6-C_1-C_2 = 117^\circ$ , c the same for the angle  $C_6-C_1-C_2 = 118.5^\circ$ , d the same for the angle  $C_6-C_1-C_2 = 120^\circ$ , e the same for an equilibrium between equal parts of the molecular models shown in fig. 3 b and fig. 3 c, both with all the angles  $C-C-C = 118^\circ$ .

$\sigma(r)/r$  curve from seven normal curves, one for each group. Each of these will have a maximum of a certain height at a given  $r$ -value, which was evaluated by adding the maxima corresponding to the single distances within the group. The resulting theoretical  $\sigma(r)/r$  curve fig. 1 b is in complete agreement with the experimental curve fig. 1 a.

This confirms the result of the last chapter, but it also plainly shows the limits of the method. It is evident from fig. 1 that, when keeping the six middle distances constant, we have a certain although limited choice of single distances in the molecule, without coming into conflict with the experimental facts. Especially is this the case if the middle distance is built up of many single distances.

A closer examination of the middle distances, however, reveals that the single distances which are of special importance for the choice of molecular structure type, are not liable to any variation of consequence. It is thus not possible to get away from:

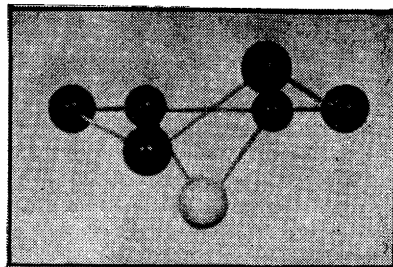


Fig. 5. Model of the 1,2-epoxy-cyclohexane molecule.

$$\text{O}-\text{C}_1 = 1.42 \text{ \AA}, \text{O}-\text{C}_3 = 3.01 \text{ \AA} \text{ and } \text{O}-\text{C}_4 = 3.35 \text{ \AA}.$$

The distances which show the greatest variability, are those embraced in the middle distance of 2.53. This uncertainty is not sufficient to make our choice of model (fig. 3 d) unreliable, but it prevents an exact determination of the angles O-C-C- and C-C-C. These angles however, cannot differ by more than a few degrees from the values given for the model fig. 3 d with an angle  $\text{C}_6-\text{C}_1-\text{C}_2 = 118.5^\circ$ .

#### SUMMARY

The molecular structure of 1,2-epoxy-cyclohexane,  $\text{C}_6\text{H}_{10}\text{O}$ , has been determined by an electron diffraction investigation of the vapour, using the rotating sector method. The resulting structure of the six-membered ring is a sort of deformed »staircase» form (fig. 5). The four C-atoms nearest to the O-atom are coplanar. The two remaining are placed one above and one below this plane. The interatomic distances and angles in this model are:

$\text{C}_1-\text{C}_2 =$	1.54 Å
$\text{O}-\text{C}_1 = \text{O}-\text{C}_6 =$	1.42 »
$\text{O}-\text{C}_2 = \text{O}-\text{C}_5 =$	2.51 »
$\text{O}-\text{C}_3 =$	3.01 »
$\text{O}-\text{C}_4 =$	3.35 »
$\text{C}_6-\text{C}_1-\text{C}_2 = \text{C}_1-\text{C}_6-\text{C}_5 =$	$118.5^\circ$
$\text{C}_1-\text{C}_2-\text{C}_3 = \text{C}_6-\text{C}_5-\text{C}_4 =$	$116.0^\circ$
$\text{O}-\text{C}_1-\text{C}_2 = \text{O}-\text{C}_6-\text{C}_5 =$	$115.0^\circ$

The two remaining C-C-C angles are  $109.5^\circ$ . The investigation leaves no doubt about the structure type, but a variation of about  $\pm 2^\circ$  in the angles mentioned above cannot be detected if the middle value of all the corresponding distances is kept constant at 2.53 Å.

The resulting structure of the six-membered ring, has a great resemblance to the six-membered ring we may expect to find in cyclohexene,  $C_6H_{10}$ , where the distance  $C_1-C_6$  must be approximately 1.34 Å and the four atoms  $C_1$ ,  $C_6$ ,  $C_5$  and  $C_6$  are necessarily coplanar.

Finally I wish to express my gratitude to Dr. O. Hassel, professor at the University of Oslo, for giving me the opportunity to carry out the foregoing work in his laboratory and for his helpful criticism and advice.

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