

## The Molecular Structure of *Cis* and *Trans* Cyclohexanediol-(1,2)

An Electron Diffraction Investigation by the Sector Method

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In previous investigations of the two isomers of cyclohexanediol-(1,2) with m.p. 99° and 104° C the structures have usually been discussed on the assumption that they are *cis/trans* isomers on the basis of a plane six-membered ring. These investigations concerned optical activity and the demonstration of different chemical reactions. The result was that the higher melting form was the *trans*-, and the other the *cis*-compound.

We now know that the cyclohexane ring is not plane. It is therefore necessary to discuss the problem from a somewhat different point of view. As early as 1930 this was pointed out by White<sup>1</sup> who avoided the designations *cis* and *trans*, and introduced Greek letters to denote the two modifications. In this investigation we will use the nomenclature introduced by Hassel for the two types of bonds in the step-formed six-membered ring,  $\epsilon$ -bonds for the six bonds from the C-atoms which are parallel to the principal axis of the carbon skeleton, and  $\alpha$ -bonds for the six bonds of the other type. In this article the two diols will be referred to by their melting points. The terms *cis* and *trans* will not be used at all.

### CHEMICAL PREPARATION

Cyclohexanediol-(1,2) m. p. 104° was prepared<sup>1</sup> by Brunel's method<sup>2</sup>. 1,2-epoxy-cyclohexane was purified by distillation and heated with water in a sealed glass tube. The diol was purified by recrystallisation from benzene. It is worth taking the trouble to purify the epoxide carefully by distillation during the preparation. By so doing the pure diol is obtained by heating with water.

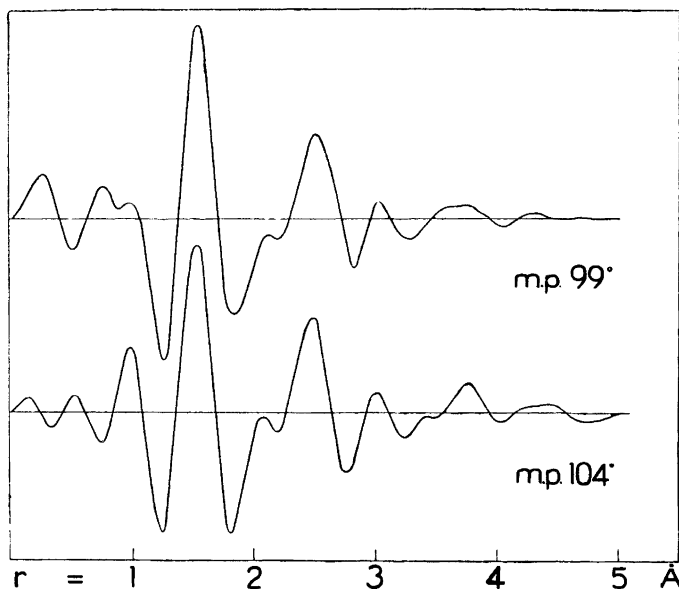


Fig. 1.  $\sigma(r)/r$ -curves of cyclohexanediol-(1,2) of m. p. 99° C and cyclohexanediol-(1,2) of m. p. 104° C (below).

Cyclohexanediol-(1,2) m. p. 99° was first prepared by Brunel's method<sup>2</sup> by treating 1-iodo-cyclohexane-acetate 2,  $C_6H_{10}IOA$ , with silver acetate in glacial acetic acid. Contrary to Brunel the diacetate of cyclohexane was not hydrolysed by potassium carbonate. The hydrolysis went much better with hydrochloric acid in absolute methyle alcohol. An attempt to prepare the diol by Markownikow's method<sup>3</sup> by oxidation of cyclohexane with potassium permanganate was very satisfactory, and the greater part of the diol was prepared in this way\*.

As a check equal quantities of the two diols were mixed together, giving the equimolecular compound with m. p. 73°.

#### ELECTRON DIFFRACTION DIAGRAMS AND DETERMINATION OF THE STRUCTURE

Several different electron diffraction diagrams were taken, using the rotating sector method. The microphotometer records revealed intensity curves in close agreement. The Fourier Analysis was based on a mean curve. The evaluated  $\sigma(r)/r$ -curves are shown in Fig. 1.

\* Markownikow's method was slightly modified. The aqueous solution containing potassium carbonate and the diol was heated over the water bath until traces of crystals appeared and was then cooled. When left over night the greater part of the liquid disappeared. The residue was extracted with boiling benzene.

From the chemical preparation of the two diols, we may presume that the two hydroxyl-groups in both isomers are in 1,2-position in relation to the six-membered ring. A number of investigations of cyclohexane and derivatives have been carried out by Hassel and his collaborators, proving that the most stable form of the six-membered ring under normal conditions is the step-form. It may especially be mentioned that the investigation of the molecular structure of 1,2-dibrom-cyclohexane <sup>4</sup> reveals the step-formed six-membered ring.

From this starting point we may form four possible structures for 1,2-cyclohexanediol. These are characterized by the connecting of the hydroxyl-groups to the six-membered ring by the following combinations of the different types of bonds:  $\kappa,\kappa$ ,  $\kappa,\varepsilon$ ,  $\varepsilon,\kappa$ ,  $\varepsilon,\varepsilon$ . If we take into consideration the ability of the six-membered ring to transpose, thereby transforming all  $\kappa$ -bonds into  $\varepsilon$ -bonds and vice versa, then only two chemically separable forms are left:

1.  $\kappa,\varepsilon$  which when transposed takes the  $\varepsilon,\kappa$ -form, which is the optical antipode of the first one.

2.  $\kappa,\kappa$  which when transposed takes the  $\varepsilon,\varepsilon$ -form. In this case two separable optically active forms are obtained.

In case 2 we have an equilibrium between two different forms of the molecule. The behaviour of the compound as one single substance is conditional on the equilibrium between the two forms being established so quickly that no chemical separation is possible. These circumstances are more closely discussed in a number of papers <sup>5</sup>.

When adjusting these two models to the two diols by use of electron diffraction, the deciding factor is the distances between the O-atoms and the C-atoms and between the two O-atoms. In order to obtain these distances an experimentally determined  $\sigma(r)/r$ -curve for cyclohexane was subtracted from the experimental  $\sigma(r)/r$ -curves of the two diols. The two difference-curves produced are shown in Fig. 2.

The distances most conducive to the formation of these curves are the above mentioned C—O and O—O distances. It must then be possible to construct the two difference curves by adding together normal curves for all the appropriate single distances <sup>6</sup>. These distances will vary according to whether the O-atom under consideration is in  $\kappa$ - or  $\varepsilon$ -position. The problem is to find out the contribution of  $\kappa$ - and  $\varepsilon$ -distances to the two curves. It may be mentioned that if the equilibrium in model 2. consists of equal parts of  $\kappa,\kappa$ - and  $\varepsilon,\varepsilon$ -forms, the whole difference between the two experimental curves will be due to the O—O distances (not taking into account the distances between the H-atom in the hydroxylgroups and the remaining atoms).

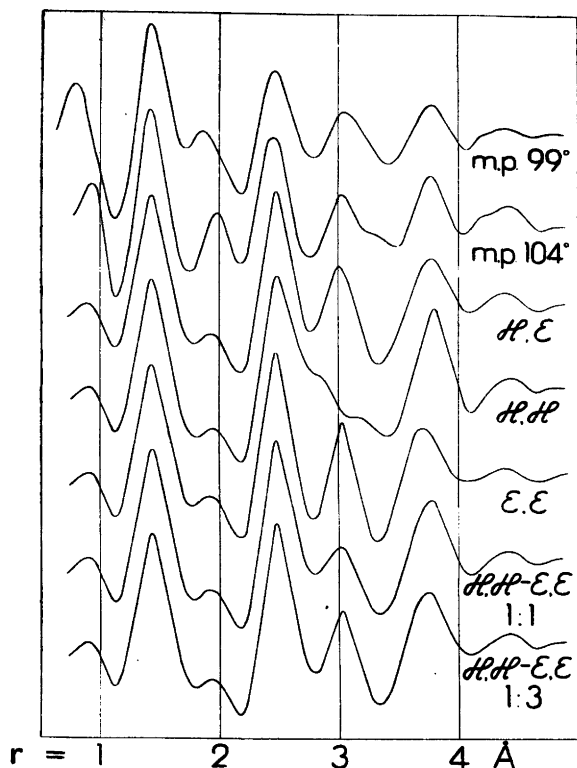


Fig. 2. Experimental difference  $\sigma(r)/r$ -curves of cyclohexanediol-(1,2) of m. p. 99° and 104° C (above). Below these two corresponding theoretical curves for molecular models with the two O-atoms in  $\kappa,\epsilon$ ,  $\kappa,\kappa$  and  $\epsilon,\epsilon$ -positions. The two last are theoretical curves corresponding to the equilibrium mixtures of the  $\kappa,\kappa$ - and  $\epsilon,\epsilon$ -models in proportions 1 : 1 and 1 : 3.

To simplify the following discussion the C-atoms are numbered as shown in Fig. 3.

In the difference curves of Fig. 2 the distinct maxima at 1.43 and 2.47 Å must correspond to the intermolecular distance O—C<sub>1</sub> and O—C<sub>2</sub>. From the

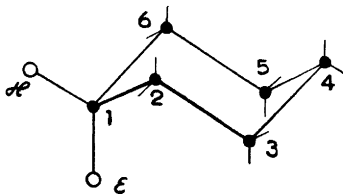


Fig. 3. Numeration of the C-atoms in cyclohexanediol-(1,2).

$\sigma(r)/r$ -curves shown in Fig. 1 we may assume the neighbouring C—C-distances to have the usual value of 1.54 Å. Applying this to the sixmembered ring we may calculate all the other distances between the atoms in the possible models of the molecule. In Table 1 the O—C-distances which correspond to the O-atom in  $\kappa$ -position and  $\varepsilon$ -position and the O—O-distances in the different cases are tabulated. Using the experimental values for the distances O—C<sub>1</sub>, O—C<sub>2</sub> and C—C given above, calculation of the angle C—C—O gives 112.5°. The angle is a little greater than the tetrahedral value (109.5°) which is quite reasonable when the effects of the Van der Waals forces between the atoms in the molecule are taken into consideration <sup>7</sup>.

Table 1. Situation of the maxima of the difference  $\sigma(r)/r$ -curves in Ångström units and the most important corresponding theoretical internuclear distances.

Diol m. p. 99° exp. maxima	Diol m. p. 104° exp. maxima	Theoretical distances		
1.43	1.43	O $\kappa$ —C <sub>1</sub> = 1.43	O $\varepsilon$ —C <sub>1</sub> = 1.43	
1.87	1.99	O $\kappa$ —H <sub>1</sub> = 1.98	O $\varepsilon$ —H <sub>1</sub> = 1.98	
2.47	2.46	O $\kappa$ —C <sub>2,6</sub> = 2.47	O $\varepsilon$ —C <sub>2,6</sub> = 2.47	O $\kappa$ —O $\kappa$ = 2.85
3.06	3.03		O $\varepsilon$ —C <sub>3,5</sub> = 3.03	O $\kappa$ —O $\varepsilon$ = 2.96
3.78	3.77	O $\kappa$ —C <sub>3,5</sub> = 3.85	O $\varepsilon$ —C <sub>4</sub> = 3.64	O $\varepsilon$ —O $\varepsilon$ = 3.73
4.40	4.43	O $\kappa$ —C <sub>4</sub> = 4.31		

In Table 1 are also shown the  $r$ -values corresponding to the maxima of the two difference curves in Fig. 2. It is easy to correlate the experimental maxima to the distances in our molecular models. This confirms our supposition that the sixmembered ring is step-formed and each O-atom placed in either  $\kappa$ - or  $\varepsilon$ -position. It is also observed that all the theoretical maxima are present, but at different heights in both the experimental curves. This means that we may expect the two diols to contain O-atoms in both the  $\kappa$ - and  $\varepsilon$ -position.

In Fig. 2 are shown the theoretical difference  $\sigma(r)/r$ -curves for the  $\kappa, \varepsilon$ -model and mixtures of different composition of the  $\kappa, \kappa$ - and  $\varepsilon, \varepsilon$ -models. These theoretical curves are constructed by using normal curves for the single internuclear distances <sup>6</sup>. It is evident that the model with both the O-atoms in  $\kappa$ -position may be excluded. The following two possible structures of the diols are then left: 1) the O-atoms are placed in  $\kappa, \varepsilon$ -position, 2) there is an equilibrium between the two models with the O-atoms in  $\kappa, \kappa$ -position and in  $\varepsilon, \varepsilon$ -position respectively, *e. g.* the two models which are transformed into each other by a transposition of the sixmembered ring. In case 2) the  $\varepsilon, \varepsilon$ -form must predominate in the equilibrium mixture.

It is difficult to correlate with any degree of certainty the two experimental difference curves in Fig. 2 and our theoretical curves. Judging from the curves

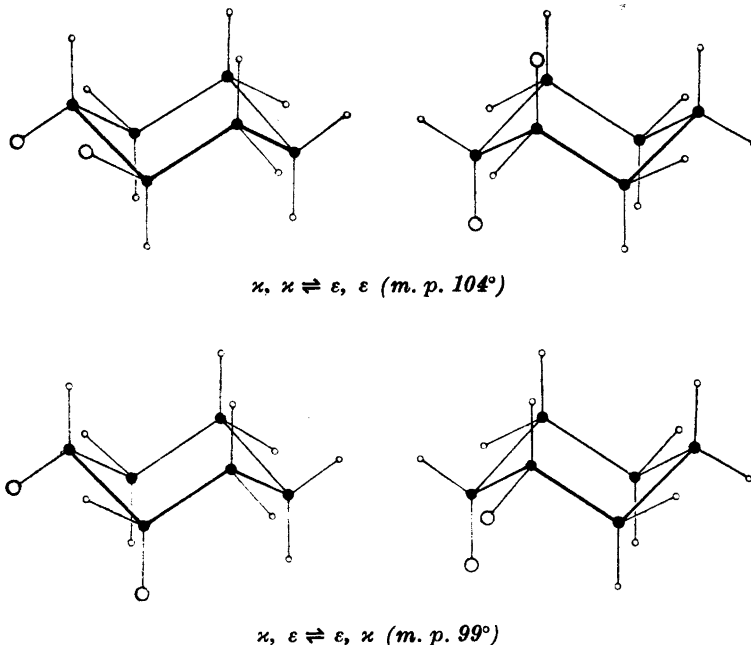


Fig. 4. Models of the two cyclohexanediols-(1,2) of m. p. 99° and 104° C.

it seems most reasonable that the  $\kappa, \varepsilon$ -model corresponds to the diol with m.p. 99°. We must bear in mind, however, that the discussion is based on difference  $\sigma(r)/r$ -curves and the reliability cannot be compared with that of ordinary  $\sigma(r)/r$ -curves. Small differences in the two curves cannot be given the same significance as in the case of ordinary  $\sigma(r)/r$ -curves.

A final conclusion, as to which of the two diols corresponds to the  $\kappa, \varepsilon$ -model and which corresponds to the  $\kappa, \kappa, \varepsilon, \varepsilon$ -mixture, must be based on the fact that the separation into optically active antipodes can be achieved in the case of the diol with m.p. 104° but not in the case of the other diol. (8). The  $\kappa, \varepsilon$ -model will consist of two optically active components in equal proportions. The transposing of the sixmembered ring will transform the d-form into the l-form and vice versa. Consequently the separation of the  $\kappa, \varepsilon$ -model into optically active antipodes will be impossible. In the case of the  $\kappa, \kappa, \varepsilon, \varepsilon$ -model, however, the conversion of the  $\kappa, \kappa$ -form into the  $\varepsilon, \varepsilon$ -form will not lead to racemisation. Thus the diol of m.p. 99° is the  $\kappa, \varepsilon$ -compound and the diol of m.p. 104° is the equilibrium mixture between the  $\kappa, \kappa$ - and  $\varepsilon, \varepsilon$ -forms. Models of the molecules are shown in Fig. 4.

## SUMMARY

An electron diffraction investigation of the vapours of the two forms of cyclohexanediol-(1,2) using the rotating sector method shows that the molecular structures of both substances are based on the symmetrical stepformed sixmembered cyclohexane ring. The diagrams indicate that one of the substances is the  $\kappa,\varepsilon$ -form, the other an equilibrium mixture of  $\kappa,\kappa$ - and  $\varepsilon,\varepsilon$ -forms. Taking the fact into consideration that the substance of m.p.  $104^\circ$  is separable into optically active antipodes, the other substance unseparable, it follows that the substance of m.p.  $99^\circ$  is the  $\kappa,\varepsilon$ -form and the substance of m.p.  $104^\circ$  is the equilibrium mixture between the  $\kappa,\kappa$ - and  $\varepsilon,\varepsilon$ -forms. Models of the molecules are shown in Fig. 4.

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