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Intra-Molecular Hydrogen Bonds in Ethylene Glycol, Glycerol, and Ethylene Chlorohydrin

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The molecular structure of ethylene glycol, glycerol, and ethylene chlorohydrin has already been studied by various investigators and from various points of view. Kohlrausch and Köppel [1] have found some anomalies in the Raman spectrum of glycol, but have not been able to determine the structure. Saksena [2] has studied the Raman spectrum of glycerol and found that no symmetry element is present in the molecule. The spectrum of ethylene chlorohydrin studied by Kohlrausch and Ypsilanti [3] gives evidence of the existence of at least *two* different space forms of this molecule. Other spectroscopic investigations have been carried out, but none of them has given decisive information about the molecular structure of the compounds in question.

From the dipole moment measurements, Zahn [4] thinks there is support for *three* different theories concerning the structure of ethylene glycol:

1) Free rotation about all the single bonds.
2) Free rotation about the carbon-oxygen bonds, but not about the carbon-carbon bond. *Trans* form.
3) Same conditions, but *cis* form.

For the ethylene chlorohydrin *two* possibilities are given:

1) Free rotation about the carbon-oxygen bond, but not about the carbon-carbon bond. *Trans* form.
2) Rigid molecule. *Cis* form.

The results of our electron diffraction investigations are not in accordance with any of these assumptions.

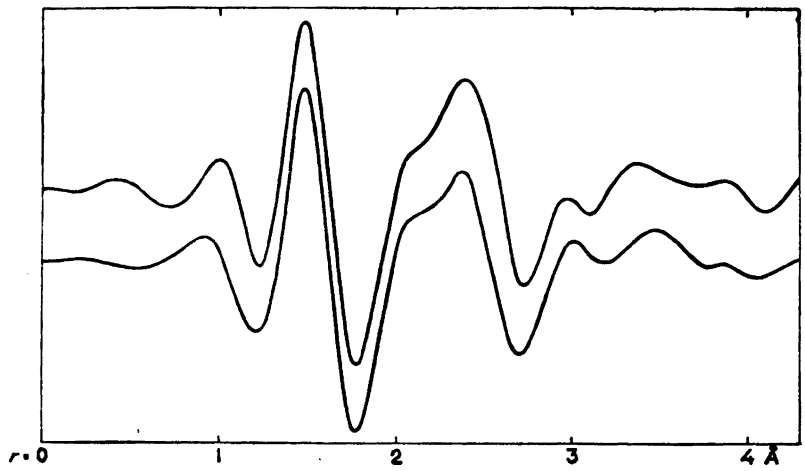

Fig. 1. Two $\sigma(r)$-curves for ethylene glycol calculated from different diagrams.

RESULTS

Ethylene glycol

In the study of the $\sigma(r)$-curve of ethylene glycol the peak corresponding to the oxygen-oxygen distance will obviously be the most interesting one. Unfortunately the contribution of this distance to the entire $\sigma(r)$-curve will be relatively small. As an additional unfavourable circumstance the peak corresponding to the oxygen-oxygen distance occurs very near a minimum caused by the neighbouring peaks. It is therefore of great importance in this case to know if the minor maxima occurring in the $\sigma(r)$-curve are real or may be explained as random errors. In Fig. 1 two $\sigma(r)$-curves for ethylene glycol are given. The lower curve has been calculated three years later than the other and from a new series of diagrams. The agreement between the two curves is a satisfactory demonstration of the reproducibility of the method. — The upper curve in Fig. 2 is the mean experimental $\sigma(r)$-curve. The dotted curve is the theoretical $\sigma(r)$-curve calculated from the Viervoll normal curves. The theoretical curve contains only such distances as are not altered by a rotation about the carbon-carbon bond. The calculation is made on the assumption of normal bond distances and valency angles (C—C = 1.54 Å, C—O = 1.43 Å, C—H = 1.08 Å, $<$C—C—O = 109.5°). The lower curve in Fig. 2 represents the difference between the experimental and the theoretical $\sigma(r)$-curve for the interval which has interest in the present connection. The highest peak in the differential curve occurring at 2.97 Å must be ascribed to the oxygen-oxygen

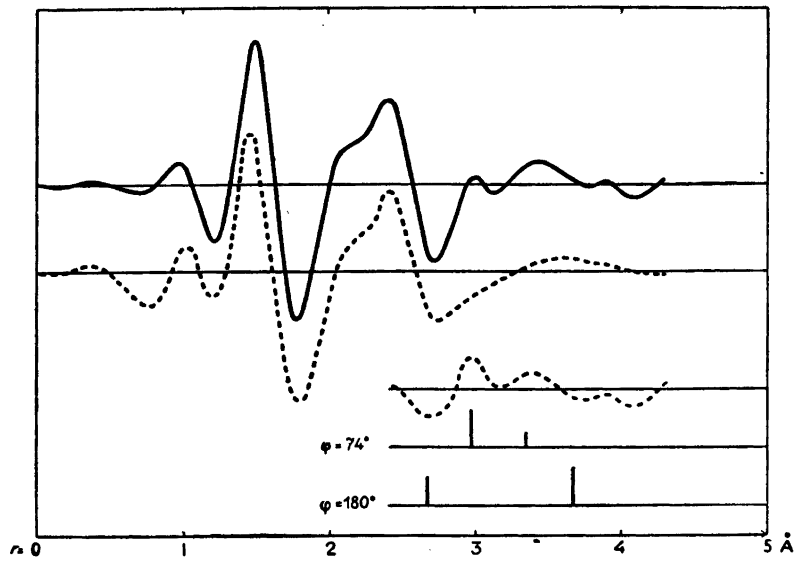

Fig. 2. Experimental, theoretical, and differential $\sigma(r)$-curves for ethylene glycol.

distance. The position of this peak corresponds to an angle φ between the two oxygen-carbon-carbon planes of 74°. The diagrams below the differential curve correspond to φ-values of 74° and 180° respectively. The exclusion of a rigid *trans*-form seems to be evident.

Glycerol

The curves given in Fig. 3 are the experimental, the theoretical, and the differential $\sigma(r)$-curves for glycerol. The curves correspond to those of ethylene glycol given in Fig. 2. The most pronounced peak in the differential curve occurs at 2.94 Å, *i. e.* — within the limits of the errors — at the same position as for ethylene glycol. The φ-value is accordingly in this case 71°. The angle φ does not, — owing to the more complex structure of the glycerol molecule, — suffice to describe the configuration unambiguously. The relative position of the two groups $H_2(OH)C$- and CH(OH)C — may be characterized by the letters α, β and γ. In the α-position the angle φ is equal to 71° and the oxygen atom in the $H_2(OH)C$-group is nearly in trans-position to the carbon atom in the —CH(OH)C-group. In the β-position the oxygen atoms are in trans-position. In the γ-position the angle φ is equal to 71° and the oxygen atom in the $H_2(OH)C$-group is nearly in trans-position to the hydrogen atom in the

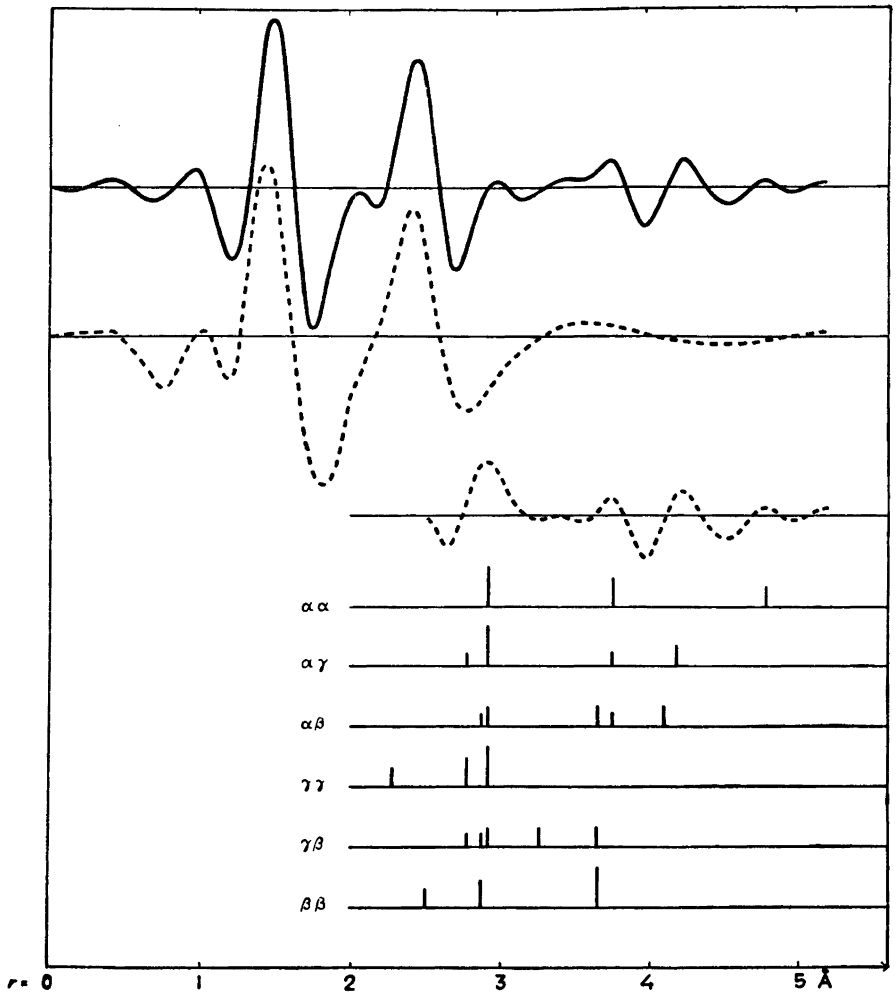

Fig. 3. Experimental, theoretical, and differential $\sigma(r)$-curves for glycerol.

—CH(OH)C-group. Though the β-position is, according to our experience concerning the glycol molecule, improbable, we shall provisionally include it. The possible configurations of the glycerol molecule are then, $\alpha\alpha$, $\alpha\gamma$, $\alpha\beta$, $\gamma\gamma$, $\gamma\beta$, and $\beta\beta$. The carbon-carbon, carbon-oxygen and oxygen-oxygen distances which might be expected in the differential curve are for all the configurations mentioned indicated in Fig. 3 by the line diagrams below the curves. From the diagrams it will be seen that all maxima in the differential curve may be

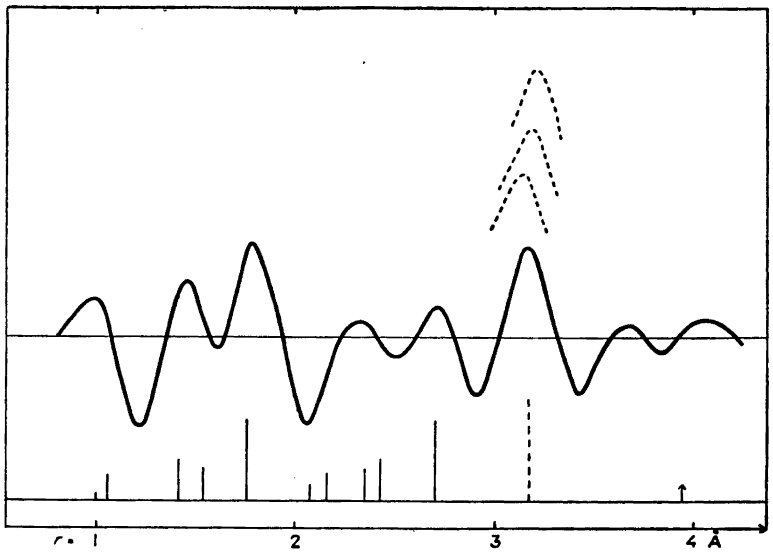

Fig. 4. $\sigma(r)$-curve for ethylene chlorohydrin.

explained assuming the two configurations $\alpha\alpha$ and $\alpha\gamma$ only. The trans-form seems therefore in this case also to be infrequent. The $\gamma\gamma$-position is improbable, because of the short 0_1—0_3-distance (2.28 Å).

Ethylene chlorohydrin

The $\sigma(r)$-curve of this compound is given in Fig. 4. In this case the most interesting distance, the chlorine-oxygen distance, must give a considerable contribution to the $\sigma(r)$-curve. The differential method is therefore unnecessary. The distances which are independent of the rotation about the carbon-carbon bond are indicated in the line diagram (solid lines). The carbon-chlorine bond distance is 1.76 Å. The other bond distances are the same as for the previous compounds. The pronounced peak at 3.17 Å must be explained as due to the oxygen-chlorine distance corresponding to a φ-value of 74°. The dotted peaks are parts of three different curves calculated from different photometer records. The φ-value varies in these three cases between 72° and 76°.

DISCUSSION

The results given above are readily explained by the assumption of intramolecular hydrogen bonds. The value of the hydrogen bond distance in ethylene glycol and glycerol of 2.96 Å $\pm$ 0.02 Å is somewhat greater than that

usually observed which vary between 2.5 Å and 2.95 Å. On the other hand, the intra-molecular hydrogen bonds assumed in our cases are not directly comparable with the common inter-molecular hydrogen bonds. In the latter the hydrogen atom is usually considered as lying on the straight line connecting the oxygen atoms. This is impossible in our case, because of steric relations. — The hydrogen bond distance between an oxygen and a chlorine atom in ethylene chlorohydrin of 3.17 Å seems fairly reasonable.

Another interpretation of the $\sigma(r)$-curve of ethylene glycol and glycerol may be mentioned: An oscillation about the carbon-carbon bonds with an amplitude of approximately 75°, and with the *trans*-position as the equilibrium position, would have resulted in a peak at 2.94—2.97 Å in the $\sigma(r)$-curve. The angular velocity is in the equilibrium position much greater than in the neighbourhood of the positions having maximal amplitudes. In the case of ethylene chlorohydrin, however, this interpretation is impossible, because of the great height of the peak at 3.17 Å. An oscillation would have decreased the height of this peak, while the actual observed height is even greater than what might have been expected from a rigid model. The assumption of an oscillation of the type mentioned must therefore, in the case of the other compounds under investigation also, be regarded as less probable than the assumption of hydrogen bonds, especially when the results of the study of ethane [5] and ethane derivatives are considered [6, 7].

A further argument based on calorimetric data is in favour of the theory of intra-molecular hydrogen bonds: In Table 1 we have listed calculated and observed values of the heats of combustion for five alcohols in the gaseous state. The calculated values are obtained in a straight forward way explained, for instance, by Wheland [8]. The experimental values are taken partly from Whelands book and partly from a work of Gallaugher and Hibbert [9]. It has been corrected for the heats of vaporization. In the fourth column the difference between calculated and observed values is given.

Table 1. Heats of combustion for some alcohols.

Compounds	Calculated	Observed	Calculated ÷ Observed
Ethyl alcohol	336.8 kcal/mol	336.8 kcal/mol	0.0 kcal/mol
n-Propyl alcohol	494.2 »	493.3 »	0.9 »
n-Butyl alcohol	651.6 »	650.0 »	1.6 »
Ethylene glycol	303.0 »	297.6 »	5.4 »
Glycerol	426.6 »	416.3 »	10.3 »

With respect to the three first compounds the difference must be regarded as zero, the deviations of the calculated values from the observed ones being

0.0 %, 0.18 % and 0.25 % respectively. For ethylene glycol and glycerol the deviations are 1.78 % and 2.42 %. This corresponds to *one* hydrogen bond within the ethylene glycol molecule and *two* within the glycerol molecule, if the hydrogen bond energy is equaled to about 5.0 kcal. This value is in good agreement with earlier observed hydrogen bond energies [10–12]. Such considerations, based on calorimetric data, must of course be treated with some caution, because of the well-known uncertainty in the determination of both calculated and observed heats of combustion and vaporization, and because of the anomalies which occur in the heats of combustion in branched hydrocarbons and non-primary alcohols.

Finally it may be mentioned that investigations on liquid ethylene glycol and glycerol by the aid of monochromatic X-rays have been carried out. These seem to lend support to our theory of intra-molecular hydrogen bonds.

SUMMARY

The structures of ethylene glycol, glycerol and ethylene chlorohydrin have been investigated by the electron diffraction sector method. Arguments in favour of the assumption of intra-molecular hydrogen bonds are given.

I should like to express my gratitude to Professor Dr. O. Hassel for his kind interest in my work and for many suggestive discussions. Without the fruitful scientific atmosphere created by him, this work would not have been accomplished. — I must also acknowledge my indebtedness to the *Fridtjof Nansens Fond* and *Det Vitenskapelige Forskningsfond av 1919* for financial aid.

LITERATURE

1. Kohlrausch, K. W. F., and Köppl, F. *Monatsh.* **65** (1935) 185.
2. Saksena, B. D. *Proc. Indian Acad. Sci.* **A 10** (1939) 333.
3. Kohlrausch, K. W. F., and Ypsilanti, G. P. *Z. phys. Chem.* **B 29** (1935) 274.
4. Zahn, C. T. *Phys. Z.* **33** (1932) 525.
5. Smith, L. G. *J. Chem. Phys.* **17** (1949) 139.
6. Hassel, O., and Viervoll, H. *Arch. Mat. Nat.-Vid.* **BXLVII** (1944) no. 13.
7. Halford, J. O. *J. Chem. Phys.* **17** (1949) 111.
8. Wheland, G. W. *The theory of resonance and its application to organic chemistry.* New York (1947).
9. Gallaugher, A. F., and Hibbert, H. *J. Am. Chem. Soc.* **59** (1937) 2521.
10. Davies, M. M. *Trans. Farad. Soc.* **36** (1940) 333.
11. Rumpf, R. *Bull. Soc. Chim. France* (1948) 211.
12. Searcy, A. W. *J. Chem. Phys.* **17** (1949) 210.

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