# *Molecular Structure Investigations by Electron Diffraction Method. II. The Molecular Structure of Ethylene Chlorohydrin*

By Mashio YAMAHA

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## Introduction

Many physico-chemical investigations such as the dipole moment measurements by C. T. Zahn[1], I. Watanabe[2], the spectroscopic studies by Kohlrauch and Ypsilanti[3], R. M. Badger[4,5], S. Mizushima et al[6,7] have shown that the ethylene chlorohydrin molecule in the gaseous state consists of two rotational isomers. Badger[5] investigated the temperature variation of the infrared and Raman spectra in relation to the intramolecular hydrogen, bonding and established the fact that, in the gaseous state, at room temperature, the molecule consists of a *trans* form and another stable one. Watanabe concluded that the latter stable form of this molecule is one for which the rotational angle $\varphi$ (see Fig. 1) is $0\sim60°$.

However, the interatomic distances, C–C, C–O, C–Cl, Cl″···O etc., cannot be determined directly by measurement of dipole moments or other spectroscopic methods. Recently, O. Bastiansen[8] determined them directly by means of an electron diffraction method using a rotating sector, as follows: C–C=1.54; C–Cl=1.76; C–O=1.43; and O″···Cl=3.17 Å. Consequently, the *gauche* form of this molecule is characterized by $\varphi=74°$.

In the discussion of the molecular structure of ethyl alcohol by M. Kimura[9], the interatomic distance C–O in this molecule was considered greater than in the case of the normal covalent bond, namely, 1.42 Å. In this report, the author has investigated the molecular parameters of ethylene chlorohydrin, and has also tried to investigate, if possible, the height of the potential barrier of internal rotation, including hydrogen bonding, in this molecule.

## Experimental Procedure

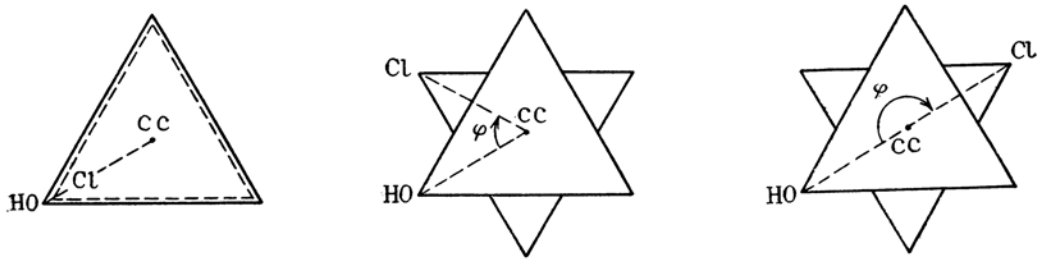
(1) *Sample.* — The commercial reagent of ethylene chlorohydrin, colored slightly yellowish, after dehydrated sodium sulphate had been immersed in it for many days, was distilled several times with a flask having a 5–10 cm. long rectifying column. The colorless viscous distillate (b. p. 128°–128.5°C) was obtained for the experiment.

(2) Details of the apparatus and methods of measurement are omitted, because they are the same as in our previous report[10].

*Apparatus*: Hot cathode, vertical type.
Camera length: 91 to 110 mm.
Wave length: 0.053–0.056 Å

The sample was spurted from the nozzle at room temperature, 25°–35°C.

The diffraction pattern thus obtained is comparatively indistinct and yet eleven diffracted




*Cis* form $\varphi=0°$ *Gauche* form $\varphi=60°$ *Trans* form $\varphi=180°$

Fig. 1. Schematic models showing the rotational angle $\varphi$ about the C–C bond for ethylene chlorohydrin molecule.

1) C.T. Zahn, *Trans. Acad. Soc.*, **30**, 804 (1934).
2) I. Watanabe, *Riken Iho* (in Japanese), **20**, 838 (1941).
3) K.W. Kohlrauch and G.P. Ypsilanti, *Z. Physik. Chem.*, **B 29**, 274 (1935).
4) R.M. Badger and S.H. Baner, *J. Chem. Phys.*, **4**, 711 (1936).
5) L.R. Zumwalt and R.M. Badger, *J. Chem. Phys.*, **7**, 87 (1939); *J. Am. Chem. Soc.*, **62**, 305 (1940).
6) S. Mizushima, Y. Morino and T. Kubota, This Bulletin, **14**, 15 (1939).
7) S. Mizushima, Y. Morino and S. Nakamura, *Sci. Papers I.P.C.R.*, **37**, 205 (1940).
8) O. Bastiansen, *Acta Chem. Scand.*, **3**, 415 (1949).
9) M. Kimura, *J. Chem. Soc. Japan* (in Japanese), **71**, 18 (1950).
10) T. Yuzawa and M. Yamaha, This Bulletin, **26** (No. 8), 414 (1953).

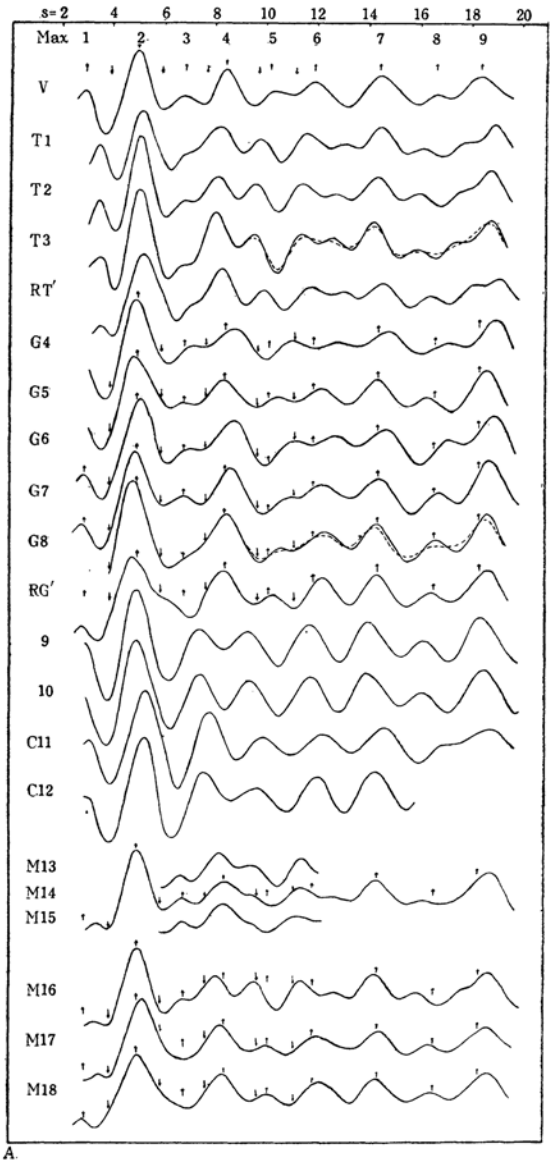



Fig. 2. Visual (V) and theoretical intensity curves for ethylene chlorohydrin molecule. (cf. Table I and II). (The curves are shown in the *s*-scale).

halos have been measured by means of a visual method up to the limit of $q<80$. The measured *s-values* (or *q-values*) of the maxima and minima are shown in Table I, and the visual intensity curves shown at the top of Figs. 2 and 3.

## Molecular Models

In constructing the assumed molecular models, the combinations of various molecular parameters have been considered and are given in Table II. First, the models were divided into several groups according to the rotational equilibrium positions about the

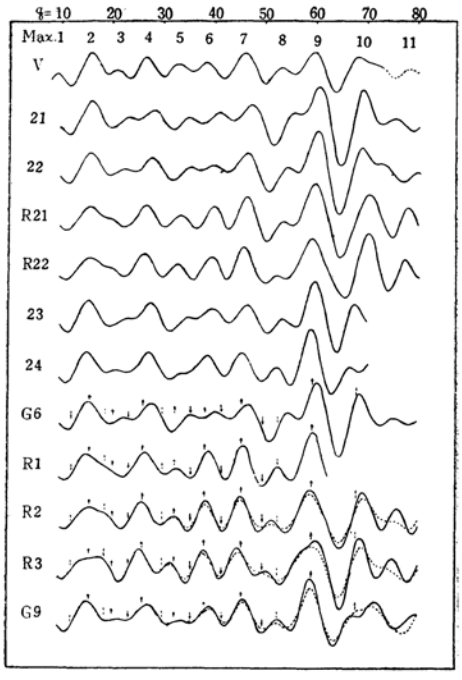



Fig. 3. Visual (V) and theoretical intensity curves for ethylene chlorohydrin molecule. (cf. Table II). (The curves are shown in the *q*-scale).

C-C bond : that is, the groups of *trans*, *gauche* and *cis* forms including the slight variations of $\varphi$ close to each form (see Fig. 1). In each groups, the interatomic distance C–O was varied from 1.43 to 1.49 Å, and the valence angles $\angle$CCCl and $\angle$CCO were varied within the range 109.5° to 112°, assuming C–H=1.09 and C–C=1.54 Å. Then assuming the other parameters inclusive of the several combinations of bond lengths, bond angles and rotational angle $\varphi$ to be constant, the mixtures of *trans* and *gauche* forms were considered (see Fig. 2). Subsequently, the bond length C–C was varied from 1.50 to 1.58 Å. Finally, in better models,the rotational angle $\varphi$ was varied from 60° to 80° (see Fig. 3).

## Intensity Curves

The theoretical intensity curves corresponding to the models mentioned above as calculated by the use of the well-known Pauling formula are given in Fig. 2:

$$I(s)=k\sum_i\sum_j Z_iZ_j\cdot\sin(sr_{ij})/sr_{ij},$$

where $s=(4\pi\sin\theta/2)/\lambda$; $\theta$, the scattering angle: $\lambda$, the wave length; and $r_{ij}$, the interatomic distance between atoms $i$ and $j$, and those as calculated by the use of Pauling-Schomaker formula in Fig. 3:

TABLE I

LIST OF MOLECULAR MODELS AND ASSUMED CORRESPONDING MOLECULAR CONSTANTS

(cf. Fig. 2) Other assumed constants: C-C=1.54 Å, C-H=1.10 Å, ∠CCH=109.5°

| Groups | Models | ($\varphi$°) | ∠CCO° | ∠CCCl° | C-O (Å) | O''···Cl (Å) |
|---|---|---|---|---|---|---|
| *Trans* | T1 | 180 | 109.5 | 109.5 | 1.43 | |
| | T2 | 〃 | 112 | 112 | 1.43 | |
| | T3 | 〃 | 109.5 | 112 | 1.49 | |
| | RT′ | 150 | 109.5 | 112 | 1.46 | 3.93 |
| *Gauche* | G4 | 60 | 109.5 | 109.5 | 1.43 | |
| | G5 | 〃 | 112 | 112 | 1.43 | |
| | G6 | 〃 | 109.5 | 109.5 | 1.46 | 3.03 |
| | G7 | 〃 | 109.5 | 112 | 1.46 | 3.09 |
| | G8 | 〃 | 109.5 | 112 | 1.49 | |
| | RG′ | 70 | 109.5 | 112 | 1.46 | 3.15 |
| Forms of $0<\varphi<60°$ | 9 | 30 | 109.5 | 112 | 1.43 | |
| | 10 | 15 | 112 | 112 | 1.43 | |
| *Cis* | C11 | 0 | 109.5 | 109.5 | 1.43 | |
| | C12 | 0 | 112 | 112 | 1.43 | |

TABLE II

LIST OF MOLECULAR MODELS AND ASSUMED CORRESPONDING MOLECULAR CONSTANTS, SHOWING THE PROPORTION OF COEXISTENCE OF TWO DIFFERENT ISOMERS (cf. Fig. 2)

| Models | Components of Two Isomer Types | Proportion % | C-O (Å) | ∠CCO° | ∠CCCl° |
|---|---|---|---|---|---|
| M13 | *Trans* and *Gauche* | 75:25 | 1.43 | 109.5 | 112 |
| M14 | 〃 〃 | 50:50 | 〃 | 〃 | 〃 |
| M15 | 〃 〃 | 25:75 | 〃 | 〃 | 〃 |
| M16 | 〃 〃 | 50:50 | 1.43 | 112 | 112 |
| M17 | *Trans* (RT′) and *Gauche* (RG′) | 20:80 | 1.46 | 109.5 | 112 |
| M18 | 〃 〃 | 50:50 | 〃 | 〃 | 〃 |

TABLE III

LIST OF MOLECULAR MODELS AND ASSUMED CORRESPONDING MOLECULAR CONSTANTS, SHOWING THE VARIATIONS OF OTHER CONSTANTS $\varphi$ AND C-C AS COMPARED WITH TABLES I AND II

Other assumed constants: C-O=1.46 Å, C-H=1.10 Å, ∠CCH=109.5°

| Models | ($\varphi$°) | ∠CCO° | ∠CCCl° | C-C (Å) | O''...Cl (Å) | $q/q_{obs}$ | Mean dev. |
|---|---|---|---|---|---|---|---|
| 21 | 60 | 109.5 | 109.5 | 1.50 | 3.01 | | |
| 22 | 60 | 〃 | 112 | 〃 | 3.05 | | |
| R21 | 70 | 〃 | 109.5 | 〃 | 3.12 | | |
| R22 | 70 | 〃 | 112 | 〃 | 3.17 | | |
| 23 | 60 | 〃 | 109.5 | 1.58 | 3.07 | | |
| 24 | 60 | 〃 | 112 | 〃 | 3.14 | | |
| G6 | 60 | 109.5 | 109.5 | 1.54 | 3.03 | 1.015 | 0.020 |
| R1 | 70 | 〃 | 112 | 〃 | 3.15 | 1.001 | 0.023 |
| R2 | 75 | 〃 | 〃 | 〃 | 3.22 | 0.995 | 0.009 |
| R3 | 80 | 〃 | 〃 | 〃 | 3.28 | 0.988 | 0.013 |
| G9 | 60 | 112 | 〃 | 〃 | 3.13 | 1.005 | 0.023 |

$$I(q)=k\sum_i\sum_j(Z_iZ_j/r_{ij})\sin(\pi qr_{ij}/10)\cdot\exp(-b_{ij}q^2),$$

where $q=10s/\pi$; and $b_{ij}$, the temperature factor.

The values of $b_{ij}$'s are shown in Table V. As regards the factor relating to the interatomic distance $O''\cdots Cl_{gauche}$, whose contribution to

TABLE IV
OBSERVED *s* AND *q-values* AND CALCULATED $q/q_{obs}$ VALUES FOR BEST MOLECULAR MODELS

| Max. | Min. | $s_{obs}$ | $q_{obs}$ | $q/q_{obs}$ R1 | $q/q_{obs}$ R2 |
|---|---|---|---|---|---|
| 1 | | (2.93) | (9.23) | | |
| | 2′ | (3.91) | (12.33) | | |
| 2 | | 5.00 | 15.84 | 0.953 | 1.007 |
| | 3′ | (5.92) | (18.84) | — | — |
| 3 | | 6.83 | 20.44 | 0.952 | — |
| | 4′ | 7.70 | 23.63 | | |
| 4 | | (8.42) | (26.22) | 1.022 | 0.995 |
| | 5′ | 9.72 | 30.06 | 1.021 | 0.988 |
| 5 | | 10.15 | 32.31 | 1.018 | 0.994 |
| | 6′ | 11.17 | 35.56 | 1.004 | 0.984 |
| 6 | | 11.90 | 38.32 | 1.019 | 1.007 |
| | 7′ | | 41.66 | 1.020 | 1.005 |
| 7 | | (14.42) | 45.59 | 1.005 | 0.995 |
| | 8′ | | 49.67 | 1.001 | 0.995 |
| 8 | | (16.67) | 52.73 | 0.998 | 0.979 |
| 9 | | 18.39 | 59.28 | 1.004 | 0.995 |
| | | Mean average: | | $1.001_4$ | $0.995_0$ |
| | | Mean deviation: | | 0.023 | 0.009 |

the intensity relations is large, the calculation was made according to the method of J. Karle[11] in consideration of the effect of the hindered rotation about the C-C bond. The details are dealt with in a later section.

To the curves T3, G8, R2, R3 and G9, the dotted curves, in which temperature factors were taken into account, are added in Figs. 2 and 3 (see later).

### Selection of the Best Model

The theoretical intensity curves of different groups which correspond to the structure of *trans*, *gauche* and *cis* forms are compared with the visual intensity curve V.

(1) In the case of *cis* form, the maximum which corresponds to the minor max. 3 of curve V does not appear and the intensity curve becomes almost sinusoidal up to $s \approx 14$.

In successive variations of the rotational angle $\varphi$ up to $\varphi = 30°$ from this *cis* position, the *s-value* of each maximum or minimum varies slightly, and the intensity curves still show simple sinusoidal features. This intensity relation is different from the actual measurement (curve V), so that the *cis* group, including the model with $\varphi = 0°$–$30°$, must be rejected.

(2) In comparing cases of the *trans* and *gauche* forms, three maxima appear between max. 4 and max. 7 in the case of the *trans* form, but two maxima appear in the case of the *gauche* form. In the case of the *trans* form, max. 3 accompanies max. 4, but in the visual curve, max. 3 seems to accompany max. 2. In this respect, the intensity relations of the visual curve are similar to those of the *gauche* form.

(3) Special attention was paid to the curves in the *gauche* group, which seem preferable for the present. The *s-values* vary slightly when the valence angle ∠CCCl is changed from tetrahedral to 112°. The *s-values* of max. 4 and max. 7 agree most closely with those of the visual curve when this angle is taken to be 112°.

Further, even when the valence angle ∠CCO is varied from tetrahedral to 112°, the variation of *s-values* is not distinct, because it seems to be obscured by the resultant intensity relation due to the variation of the O″···Cl distance and other distances.

(4) As the C–O distance is extended from 1.43 to 1.49 Å, max. 3 acquires a shelf-like feature, approaches max. 4, and almost disappears as shown in curve G8. Furthermore, the *s-value* for each maximum does not coincide with the actual measurement.

The above-mentioned discussion cannot be made independently in regard to the variations of each parameter. Since no satisfactory result has been obtained thus far as shown in Fig. 2, cases wherein the *trans* and *gauche* forms coexist and cases wherein C–C=1.50 and C−C=1.58 Å have been examined (see Figs. 2 and 3).

(5) The curves in which the *trans* and *gauche* forms are mixed are M13∼M18 of Fig. 2 (see Table II).

The result does not necessarily coincide with the actual measurement, but it shows better agreement. Recently S. Mizushima and collaborators confirmed the co-existence of rotational isomers through the analyses of Raman- and infrared spectra, and our result coincides with theirs in general. The visual intensity curve is close to that of the *gauche* form; so that, in view of the ratio of mixing at room temperature, the *gauche* form may be considered predominant.

(6) Good results have been obtained by taking the co-existence of the *trans* and *gauche* forms into consideration, but, on account of the intensity relation of max. 5 and max. 6 in the actual measurement, the models were not sufficient. Therefore, assuming tentatively that the *trans* and *gauche* forms do not co-exist, that is, that the molecule exists in only one form, further investigations have been made in cases of $\varphi = 70°$, 75°, 80°, and 150° (Fig. 3—the curves G6, R1, R2, R3, G9).

11) J. Karle, *J. Chem. Phys.* **15**, 202 (1947).

Upon varying $\varphi$ from 70° to 80°, the shelf-like feature appears in max. 2 and 3, but this intensity relation is not apparent in the actual measurement. Max. 5 shifts towards a smaller *s-value* than in the case of the *gauche* form, so as to coincide with the visual curve. This tendency is similar to cases of C–C=1.50 Å, $\varphi$=70° (see curves R21 and R22).

O. Bastiansen reported that the rotational angle $\varphi$ of the *gauche* form has been determined to be 74°. In our investigation, the curve $\varphi$=75° seems to show very excellent agreement with the actual measurement (see curve R2 in Fig. 3).

(7) In the cases of C–C=1.50 and 1.58 Å, the curves 21 to 24 of the *gauche* form are shown in Fig. 3. Their intensity relations are mostly not different from those of the *gauche* form in Fig. 2, but the *q-value* of each maximum or minimum changes appreciably. By assuming $\varphi$=70°, the *s-values* (*q-values*) of max. 3 and max. 5 and their intensity relations are in better agreement than by assuming the *gauche* form ($\varphi$=60°).

## Radial Distribution Curve

The radial distribution curve has been calculated by using the following formula:

$$rD(r)=\sum_{q=1}^{q=\max} I(q)\cdot\sin(\pi qr/10)\cdot\exp(-aq^2),$$

where the $a$ is determined to be $\exp(-aq_{\max}^2)=0.1$, $q_{\max}$ being the largest *q-value* observed (about $q_{\max}=80$) in the actual measurement. For the numerical function $I(q)$, the visual intensity curve has been used.

Each maximum (peak) of radial distribution curve (Fig. 4) is interpreted as follows:

1.46 Å=C–O, 1.76 Å=C–Cl,
2.75 Å=C′···Cl, 3.10 Å=O″···$Cl_{gauche}$.

Maxima other than the above-mentioned are considered to be the superpositions of maxima of corresponding interatomic distances, and they are difficult to separate individually. Further, a maximum, though not sufficiently distinct, appears close to $r$=3.90 Å, which is supposed to be due to the co-existence of a *trans* form.

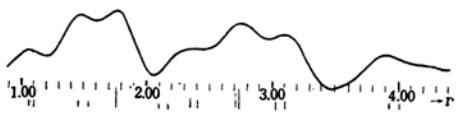



Fig. 4. Radial distribution curve for ethylene chlorohydrin molecule.
The interatomic distance corresponding to each peak is shown under the curve.

The distance which corresponds to the O″···Cl in this *trans*-form seems slightly shorter than the calculated O″···$Cl_{trans}$ (about 4.13 Å). If this distance is considered for the moment to be correct, the following three conditions can be given;

(1) Angle $\varphi<180°$,
(2) Valence angles ∠CCO, and ∠CCCl may be smaller than 112°,
(3) Bond length C–C<1.54 Å.

## Calculation of Temperature Dependence Affecting the Intensity Curves

According to the report by J. Karle, in the case of the $XY_2C$–$CY_2X$ type molecule, the contribution of each atom pair X″···X to the intensity curve is represented by the following formula, in which the variation of the following intensity relation caused by the restricted rotation about the C–C single bond in the vicinity of the "*gauche*" form is taken into consideration:

$$(\cos\Theta)^{1/2}\sin[\tau_1-(\gamma^2\tau_1\cdot\sin^2\Theta/4\beta)+\Theta/2]\times\exp[-\gamma^2\tau_1\cos^2\Theta/4b^2]/\tau_1, \quad (1)$$

where: than $\Theta=\beta\tau_1/b^2$,

$\beta=C_2/[8(C_1-C_2/2)]-3[C_2/(C_1-C_2/2)]^2/32$,
$b^2=\alpha\tanh(h\nu/2kT)$, $\nu=\sigma(V_0/2I)^{1/2}/2\pi$,
$\tau_1=s(C_1-C_2/2)^{1/2}$, $\alpha^2=2\sigma^2\pi^2IV_0/h^2$,
$\sigma=3$,
$I=\sum mr^2=I_1I_2/(I_1+I_2)$,
$\gamma=\sqrt{3}C_2/[4(C_1-C_2/2)]$,
$C_1=(l_1^2+l_2^2)/2$,
$C_2=(l_1^2-l_2^2)/2$, $s=(4\pi\sin\theta/2)/\lambda$*,

and where $V_0$ is the assumed potential barrier of the hindered rotation about C–C bond. In the case of the ethylene chlorohydrin molecule, $V_0$ includes the potential

TABLE V
APPROXIMATE TEMPERATURE FACTORS USED FOR EACH ATOM PAIR EXCEPT THAT OF O′′···Cl (For the factor $\exp(-b_{ij}q^2)$ in pauling-schomaker formula

| Atom Pairs | $r_{ij}$(Å) | $(\pi^2/200)<l_{ij}^2>_{av.}$ | $b_{ij}$ (used) |
|---|---|---|---|
| C–H | 1.10 | 0.00030 | 0.00015 |
| C–O | 1.43–1.49 | 0.000145 | 0 |
| C–C | 1.50–1.58 | 0.000148 | 0 |
| C–Cl | 1.74–1.80 | 0.000139 | 0 |
| O′···H | (2.10) | 0.00041 | 0.00026 |
| C′···H | (2.17) | 0.00037 | 0.00022 |
| Cl′···H | (2.35) | 0.00053 | 0.00037 |
| C′···O | (2.44) | 0.00022 | 0.00007 |
| C′···Cl | 2.67–2.78 | 0.00022 | 0.00007 |
| O″···$H_g$ | | | 0.0008** |
| O″···$H_t$ | | | 0.0006** |
| Cl″···$H_g$ | | | 0.0006** |
| Cl″···$H_t$ | | | 0.0004** |

** Roughly assumed values.

TABLE VI

NUMERCIAL VALUES IN FORMULA (1) RELATING TO THE ESTIMATED HINDERED-ROTATIONAL POTENTIAL BARRIER $V_0$ CORRESPONDING TO THE ATOM PAIR $O''\cdots Cl_{gauche}$ FOR ETHYLENE CHLOROHYDRIN (C–Cl=1.77 Å assumed)

| $V_0$ kcal./mol. | $\tau_1$ | $\gamma^2$ | $\gamma^2/4b^2$ | C–O (Å) | ∠CCO° | ∠CCCl° |
|---|---|---|---|---|---|---|
| 3 | 3.0943 s | $0.0439_3$ | $0.00098_7$ | 1.48 | 109.5 | 112 |
| 5 | 〃 | 〃 | $0.00059_4$ | 〃 | 〃 | 〃 |
| 10 | 〃 | 〃 | $0.00030_3$ | 〃 | 〃 | 〃 |
| 20 | 〃 | 〃 | $0.00014_3$ | 〃 | 〃 | 〃 |
| 3 | 3.0789 s | $0.0408_4$ | $0.00091_8$ | 1.43 | 〃 | 〃 |
| 10 | 〃 | 〃 | $0.00028_2$ | 〃 | 〃 | 〃 |

energy of hydrogen bonding. (In other words, it includes, in the *gauche* form, the portion of the potential energy caused by the hydrogen bond O–H···Cl.) $l_1$ is the largest interatomic distance of X''···X (i.e. at the *trans* position) and $l_2$ the smallest (i.e. at the *cis* position). $I_1$ and $I_2$ are the moments of inertia of the atoms X's (that is, atoms O and Cl in our case respectively) around the axis C–C, $h$ is Planck's constant and $k$ is Boltzmann's constant. The computed values $\tau_1$, $\gamma^2$ and $\gamma^2/4b^2$ in the case of the ethylene chlorohydrin molecule are shown in Table VI with the assumed values $V_0$, C–O (Å), ∠CCO° and ∠CCCl°.

Strictly speaking, however, this formula is originally to be applied to the case in which two X-atoms are the same, for instance, the case of 1,2-dichloroethane molecule, which has a threefold symmetry axis, namely $\sigma=3$. When the restricted rotation of this molecular type becomes infinitesimal, that is, the molecule is assumed to be rigid, the formula (1) approaches the form:

$$(\sin sl_{ij})/sl_{ij}. \qquad (2)^*$$

In the strict calculation of the contribution of intensity variations made by the restricted rotation, all atomic distances whose variations contribute to the intensity variations should be taken into account (that is, the distances assigned to the form Y''···Y, Y''···X). Because the two X atoms are O and Cl in our case, that is, not identical, and also because similar calculation regarding the other interatomic distances Cl''···H, O''···H, and H''···H etc., whose contributions may be appreciable but have actually been neglected, the approximation resulting from the application of this principle proposed by J. Karle may be considered comparatively rough for our case of the ethylene chlorohydrin molecule.

* Since the $\tau_1$ in the formula (1) corresponds to $sl_{ij}$ of the formula (2), the part of $(\cos\theta^{1/2}\cdot\sin(\cdots\cdots)$ in the former approaches $(\sin sl_{ij})/sl_{ij}$ and the part of the exponential approaches 1 in the latter.

Assuming the approximations in our case to be admissible, the contributions have been calculated for the cases in which $V_0$ is chosen as 3, 5, 10 and 20 kcal./mol. It has been found that $V_0$ is about 10 kcal./mol. or more as a result of the comparisons of the observed intensity relations. The dotted lines on the curves T3, G8, G9, R2 have been calculated for the presumed $V_0$ value. If the value $V_0$ is assumed to be $V_0<10$ kcal./mol., the curves become of a very much more damped form in the range $q>50$, and it would become impossible to observe clearly the maxima which can actually be detected in this range of our experiment.

## Discussion and Summary of Results

From the above considerations, the intensity curves RG', R1, R2, R21, R22, M17 and M18 seem to be nearly satisfactory, and thus the final results of the molecular structure of ethylene chlorohydrin have been obtained as follows:

C–O=1.46 Å±0.02 Å, O''···Cl=3.20 Å±0.06 Å,
∠CCCl=111°±2°, ∠CCO=110°±2°.

The stable form of the internal rotation about the C–C bond seems to be nearly a *gauche* form, that is, the exact position $\varphi=75°$ is regarded as the most reasonable one from the overall intensity relation of diffracted pattern.

These results are considered to agree with those from the electron diffraction method using a rotating sector by O. Bastiansen[8] and also with those from the dipole moment measurement[2].

From the analysis of the radial distribution curve and of the intensity curves, the *gauche* ($\varphi=75°$) and *trans* forms might be supposed to co-exist, and this has been confirmed from the spectroscopic results, but the proportion of these co-existing forms has not been determined from our study.

The fact that the *gauche* form is predominant at room temperature is thought to be caused by the formation of the intramolecular

hydrogen bond[12]. The potential $V_0$ of the internal hindered rotation including the contribution of the hydrogen bond is presumed to be approximately from 7 to 10 kcal./mol. or more, as judged from the examination of the approximate calculation and of the degree of damping of the experimental intensity curve.

It would be very interesting, but hardly possible, to determine $V_0$ precisely by an experimental method other than the electron diffraction. Even by the electron diffraction method (using the visual method), it is very difficult to confirm precisely the height of the potential barrier of internal hindered rotation to which the intramolecular hydrogen bond contributes, because the variation of the intensity relation is not so obvious as to allow conclusions in the order of several kcal. per mol.

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*Chemical Institute, Faculty of Science*
*Tokyo University of Education*
*Ootsuka, Tokyo*

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