Molecular Structure Investigations by Electron Diffraction Method. IV. The Molecular Structures of α, γ-Dichlorohydrin and Ethylene Cyanohydrin

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Introduction

The molecular structure of ethylene chlorohydrin has been surveyed by S. Mizushima[1-4] by means of infra-red and Raman spectra studies in regard to the problems of energy and entropy differences between the two intramolecular rotational isomers, i.e., the *trans* and the *gauche* forms of this molecule.

According to the surveys by O. Bastiansen[5] and by the author[6] using an electron diffraction method, a considerable fraction of the molecules in the gaseous state exist in the *gauche* form, in which the intramolecular hydrogen bond is formed between the O and Cl atoms. Previously, Zumwalt and Badger[7], by using infra-red spectroscopic data, established the fact that each of the ethylene chloro-, bromo- and iodo-hydrin, and α, γ-dichlorohydrin molecules, all of which have -O-H radicals, forms an intramolecular hydrogen bond between the oxygen and halogen atoms. Since the publication of the previous report[6], surveys have been continued on the molecular structures of α, γ-dichlorohydrin (1, 3-dichloropropanol (2)) and ethylene cyanohydrin (Hydracrylonitrile) by using the visual electron diffraction method. As to the structure of ethylene cyanohydrin, the molecule does not seem to form the intramolecular hydrogen bond, and the question, in what stable position the molecule exists in a gaseous state, has been examined.

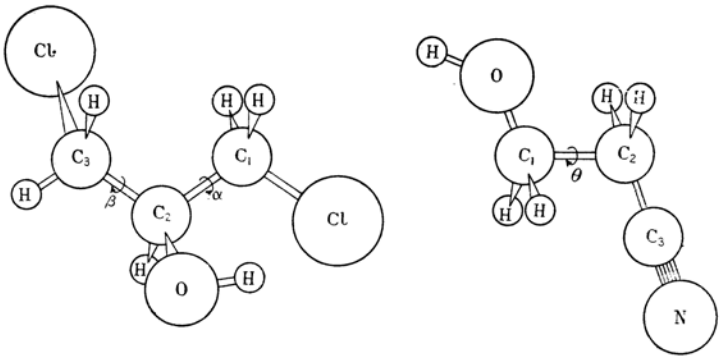
Experimental Procedure

1) Apparatus. — The electron diffraction apparatus of the vertical, hot cathode type was described in the previous publication[8] (camera length: 91 mm. and 101 mm.).

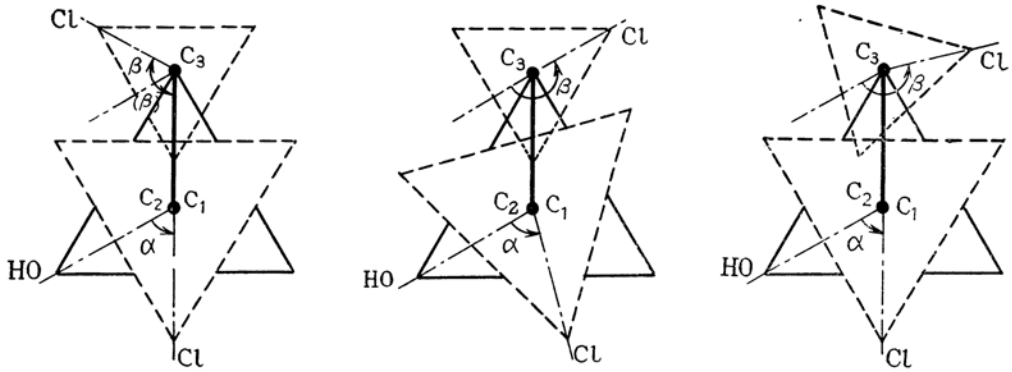
The samples are viscous liquids and they show high boiling points. They were spurted from the high temperature nozzle having a nichrome-wire heating device.

2) Samples.—*α, γ-Dichlorohydrin.*—A commercial sample was purified by distillation under reduced pressure (boiling point: 87°C/35 mmHg).

1) S. Mizushima, Y. Morino and T. Kubota, *Bull. Chem. Soc. Japan*, **14**, 15 (1939).
2) S. Mizushima, Y. Morino and S. Nakamura, *Sci. Paper I.P.C.R.*, **37**, 205 (1940).
3) S. Mizushima et al., *J. Chem. Phys.*, **19**, 1477 (1951).
4) S. Mizushima et al., *J. Am. Chem. Soc.*, **74**, 1378 (1952).
5) O. Bastiansen, *Acta Chim. Scand.*, **3**, 415 (1949).
6) M. Yamaha, This Bulletin, 29, 865 (1956).
7) L.R. Zumwalt and R.M. Badger, *J. Am. Chem. Soc.*, **62**, 305 (1940); *J. Chem. Phys.*, **7**, 87 (1939).
8) T. Yuzawa and M. Yamaha, This Bulletin, **28**, 414 (1953).



α, γ-Dichlorohydrin Ethylene Cyanohydrin



α=60°
β=−60° (or β′=+60°)
(cf. curve G or H)

α=75°
β=180°
(cf. curve N)

α=60°
β=165°
(cf. curve K)

α, γ-Dichlorohydrin

Fig. 1. Schematic models which show the relative atomic configulations for α, γ-dichlorohydrin and ethylene cyanohydrin molecules.

The relative position between O and two Cl atoms of each form varying according to the internal rotation about C-C bonds, is also shown at the lower position for the dichlorohydrin molecule.

TABLE I

THE LIST OF MOLECULAR MODELS AND CORRESPONDING MOLECULAR PARAMETERS OF α, γ-DICHLOROHYDRIN

Models	∠CCC°	∠CCCl°	α°	β°	C–Cl	C′′···Cl$_g$	C′′···Cl$_t$	O′′···Cl$_g$	O′′···Cl$_t$	Cl′′′···Cl
A	109.5	109.5	60	180	1.77	3.08	4.09	3.03	4.01	4.52
B	〃	112	〃	〃	〃	3.13	4.12	3.09	4.03	4.76
C	112	〃	〃	〃	〃	3.17	4.14	〃	〃	4.73
D	109.5	109.5	〃	150	〃	2.77	4.09	3.03	3.93	4.49
E	〃	112	〃	〃	〃	2.84	4.12	3.09	3.96	4.56
F	〃	109.5	〃	120	〃	3.78	4.09	3.03	3.71	4.93
G	〃	〃	〃	+60	〃		〃	〃		5.40
H	112	112	〃	−60	〃	3.17	4.14	3.09		4.81
I	〃	〃	45	180	〃	3.13	4.13	2.93	4.03	4.80
J	〃	〃	60	〃	1.75	3.17	4.12	3.08	4.01	4.70
K	109.5	〃	〃	165	1.77	2.97	〃	3.09	4.03	4.66
L(=B)	〃	〃	〃	180	〃	3.13	〃	〃	〃	4.76
M	〃	〃	〃	195	〃	3.31	〃	〃	〃	4.90
N	〃	〃	75	180	〃	3.13	4.10	3.22	〃	4.60
O	〃	109.5	60	〃	1.80	3.09	4.12	3.05	〃	〃

TABLE II

THE LIST OF MOLECULAR MODELS AND CORRESPONDING MOLECULAR PARAMETERS OF ETHYLENE CYANOHYDRIN

Models	∠CCC°	θ°	C_1–C_2	C_2–C_3	C≡N (Å)	O″…C (Å)	O‴…N (Å)
A	109.5	180	1.54	1.54	1.16	3.79	4.88
B	〃	〃	〃	1.50	〃	3.76	4.85
C	112	〃	〃	〃	〃	3.78	4.86
D	109.5	〃	1.52	1.46	1.20	3.70	4.83
E	〃	〃	〃	1.42	1.16	3.67	4.76
F	〃	60	1.54	1.50	〃	2.88	3.63
G	112	〃	〃	〃	〃	2.93	3.70
H	109.5	〃	1.52	1.46	1.20	2.84	3.62
I	〃	0	1.54	1.50	1.16	2.52	3.13
J	112	〃	〃	〃	〃	2.59	3.21

Ethylene Cyanohydrin.—A sample synthesized from ethylene bromohydrin by Mr. Kubouchi of the Electrical Communication Laboratory has been used (boiling point: 108°/12 mmHg).

3) Electron Diffraction Patterns. — The maxima and minima of diffracted halos appearing on photographic plates have been measured visually. For dichlorohydrin, nine distinct halos have been observed in the range of $q<80$ in addition to several faint or indistinct halos. For ethylene cyanohydrin, eight halos including weak and indistinct ones have been observed in the range of $q<60$. Measured *q-values* of maxima and minima are shown in Tables IV and V, and visual intensity curves are shown at the top of Figs. 2 and 4, followed by the theoretical intensity curves.

4) Theoretical Intensity Curves and Radial Distribution Curves.—The theoretical intensity curves have been calculated by using the following well-known Pauling-Schomaker formula;

$$I(q)=k\sum_i\sum_j (nZ_iZ_j/r_{ij})\cdot\sin(\pi q r_{ij}/10)\cdot\exp(-b'_{ij}q^2),$$

where, $q=10\,s/\pi$; $s=(4\pi\sin\theta/2)/\lambda$; θ, the scattering angle and λ, the wave length of the beam.

The molecular parameters which are used in the construction of models are listed in Table I for dichlorohydrin and in Table II for cyanohydrin (cf. Fig. 1).

TABLE III

TEMPERATURE FACTORS b'_{ij} FOR THE CALCULATION OF INTENSITY CURVES OF α, γ-DICHLOROHYDRIN MOLECULE

Atompairs	b'_{ij}
C–H	0.00015
C–O	0
C–C	0
C–Cl	0
C′…H	0.00022
C′…O	0.00008
C′…C	0.00017
C′…Cl	0.00008
Cl′…H	0.00040
C″…Cl_g	0.00050
Cl″…O_g	0.00040
C″…Cl_t	0.00040
Cl″…O_t	0.00033
Cl‴…Cl	0.00070

For dichlorohydrin, the temperature factors b'_{ij}, whose values are suggested from the case of

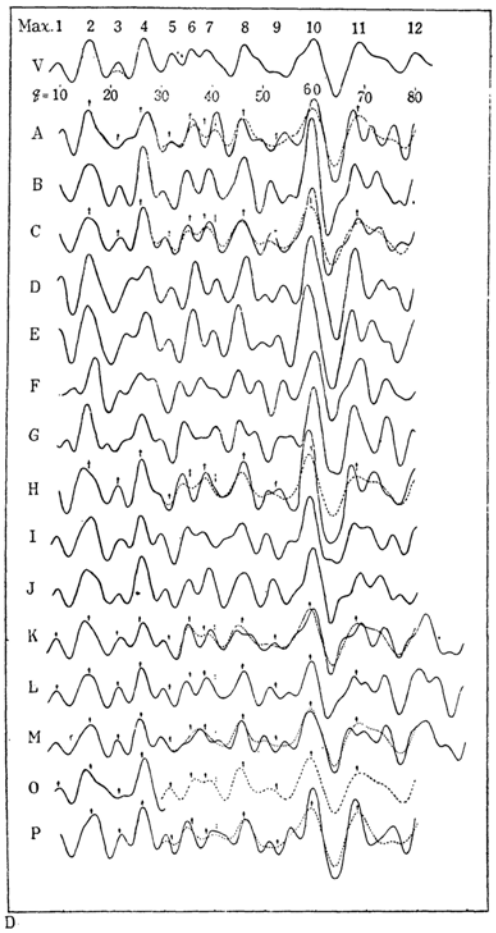


Fig. 2. Visual (V) and theoretical intensity curves for dichlorohydrin molecule.
Dotted curves correspond to the curves in which the temperature factors for each atomic distance as shown in Table III are taken into consideration.

ethylene chlorohydrin[9] and are listed in Table III, are taken into consideration, the corresponding curves being shown by dotted curves in Fig. 2.

For ethylene cyanohydrin, the temperature factors are ignored in the approximate calculation, since the observed intensity curve extends to $q<60$.

Also the radial distribution curves using the visual intensity curves have been calculated by means of the following formula;

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

and are shown in Figs. 3 and 5.

5) Analyses of Intensity Curves and Radial Distribution Curves.—a) α,γ-Dichlorohydrin.— In constructing the molecular models, the following parameters are assumed (i), and varied in the ranges (ii):

(i) C-C=1.54 Å, C-O=1.45 Å, C-H=1.10 Å ($Z_H=1.2$),

(ii) C-Cl=1.75 Å~1.80 Å, ∠CCC=109.5°~112°, ∠CCCl=109.5°~112°.

TABLE IV

OBSERVED *q-values* AND CALCULATED q/q_{obs} VALUES FOR BETTER MOLECULAR MODELS OF α,γ-DICHLOROHYDRIN

Max.	Min.	q_{obs}	q/q_{obs} N	C	O
2		16.07	0.996	0.989	0.989
	3′	(19.70)	—	0.990	0.990
3		21.54	(1.040)	1.003	1.010
	4′	23.47	0.997	1.010	0.999
4		26.12	1.015	0.999	0.995
5		31.70	0.987	0.962	0.962
6		35.90	1.008	0.987	0.972
7		(38.72–40.93)			
		(39.82)	1.008	(0.989)	0.997
8		46.41	0.978	0.989	0.991
9		(52.85)	(0.967)	0.973	—
10		59.68	0.995	0.999	0.994
11		68.53	1.008	1.007	0.998
Mean deviation:			0.999_1	0.991_4	0.990_6
Mean sq. average deviation:			0.011_2	0.012_5	0.012_5

9) For molecules having C≡N triple bond, the distance C≡N seems reasonably to be 1.16Å; that is, for example, for methyl cyanide, $CH_3-C\equiv N$,
C≡N=1.16Å by L.O. Brockway, *J. Am. Chem. Soc.*, 58, 2516 (1936).
C≡N=1.16Å and C–C=1.49Å by L Pauling et al., *J. Am. Chem. Soc.*, 61, 927 (1939).
$r_{C\equiv N}$=1.157Å (HCN),
1.163Å (Cl–CN),
1.160Å (Br–CN),
1.159Å (I–CN), by means of microwave spectra by W.J.O. Thomas, *J. Chem. Phys.*, 19, 1162 (1951),
for Acrylonitrile $CH_2=CH^*-C\equiv N$
$C^*-C=1.44$Å and C≡N=1.16Å.
by T. Saito, reported in the Ann. Meeting of the Chem. Soc. Japan, (1954), April.

TABLE V

OBSERVED *q-values* AND CALCULATED q/q_{obs} VALUES FOR THE BEST MODEL OF ETHYLENE CYANOHYDRIN

Max.	q_{obs}	q/q_{obs} E
(shelf)	13.14	0.989
2	18.00	1.014
(shelf)	21.78	1.010
3	25.86	1.025
4	30.68	0.999
5	34.13	1.002
6	40.40~	0.990
	43.78	0.984
7	49.22	(1.034)
8	55.73~	1.005
	59.00	1.012
Mean deviation:		1.003
Mean sq. average deviation:		0.012_2

In this case, since the molecule has a complicated structure, the values of parameters are confined to the narrower range of variation referring to the values of ethylene chlorohydrin previously determined. It was established that considerable fraction of the ethylene chlorohydrin molecules have the structure of *gauche* form, that is, the structure in which the intramolecular hydrogen bond is formed between Cl and O atoms even at room temperature, the rotational angle α of *gauche* form being about 75°.

The dichlorohydrin molecule has two O···Cl atom pairs, the combinations of two rotational equilibrium angles α and β (see Fig. 1) around the two C-C bonds being taken up as shown in the fourth and fifth columns of Table I, in which atomic distances and valence angles corresponding to each model are listed.

The ranges of variations of angles α and β are as follows*:

α=45°, 60° (*gauche*), 75°.

$\beta=\pm60°$ (*gauche*), 120°, 150°, 165°, 180° (*trans*) and 195°.

(1) As the angles ∠CCC and ∠CCCl are varied from 109.5° to 112°, the *q-values* of maxima 5, 6 and 7 decrease slightly. The intensity relations of maxima 2, 3 and 4, and those in the range $45<q<60$ differ from one another in the curves A, B and C. Also, in the curves D and E, the *q-values* of maxima 4, 5, 6, 7, 8 and 9 decrease according to the similar variation of parameters. The intensity relations and *q-valus* of the models having both 112° of angles ∠CCC and ∠CCCl are clearly different from those of the visual curve.

(2) As the C-Cl distances are changed from 1.75 Å to 1.80 Å, the *q-values* of the maxima and minima change slightly, and the height of maximum 7 becomes lower. However, the intensity relations and *q-values* of maxima 5, 6 and 7 for

* In the combinations of angles α and β, obviously, a model having α=60°, β=180° and one having α=180°, β=60°, are equivalent.

both models J and P are unsatisfactory, although model O seems better.

(3) If one of the two O···Cl pairs forms the intramolecular hydrogen bond, i.e. with the angle $\alpha \approx 60°$, the other O···Cl pair seems unable to form another hydrogen bond, and consequently the rotational angle $\beta = \pm 60°$ seems inadequate. This fact is made clear from the comparisons of the curves G ($\alpha = 60°$, $\beta = 60°$) and H ($\alpha = 60°$, $\beta = -60°$) with the curves A, B and C, each of which has the combination of $\alpha = 60°$, and $\beta = 180°$.

In the curves G and H, maximum 5 accompanies maximum 4 and shows shelf-like feature, especially in the curve G, the intensity relation seems clearly different from that of the visual one, and also the maxima 6 and 7 shift inward for curve H.

(4) Assuming one O···Cl pair is in a position of $\alpha = 60°$, the relative position of the other O···Cl pair is examined by varying the angle $\beta = 120°$, 150°, 165°, 180° and 195°. In the curves D and E ($\beta = 150°$), maximum 3 accompanies maximum 4 with a shelf-like feature. The curve F ($\beta = 120°$) illustrates the extreme feature in which both maxima 3 and 5 come together with maximum 4 and show deterioration. In the curve M ($\beta = 195°$), the maxima 3, 4, 5 and 8 shift inward, and maxima 6 and 7 seem to become one maximum. In the curves K and L, the intensity relations and the positions of maxima of over-all q-range become better and nearly adequate, but maximum 5 is situated at a smaller *q-value* than the visual curve, in which minimum 5′ seems to be deeper than minimum 6′ and maximum 5 comes comparatively near maximum 6.

(5) In the case of ethylene chlorohydrin, the rotational angle α relating to one O″···Cl atom pair in the vicinity of *gauche* position was shown to be 75°. Consequently, in the case of this molecule, the combination of $\alpha = 75°$ and $\beta = 180°$ is considered as shown in the curve N. The intensity relations for the entire q-range, except maximum 3, and the *q-values* of the maxima and minima of this curve coincide with those of the visual curve.

(6) The radial distribution curve (Fig. 3) computed by using the experimental intensity curve has been analyzed into various corresponding peaks, and several peaks corresponding to the distances of atom pairs are as follows:

Peak A: 1.15 Å = C–H (a little longer)
B: = C–O and C–C
C: 1.77 Å = C–Cl
D: = O′···H and C′···H
E: = Cl′···H, C′···O, C′···C
F: 2.71 Å = C′···Cl
G: = C″···Cl, O″···Cl (in the vicinity of the *gauche* position)
H: = C″···Cl, O′···Cl (in the vicinity of the *trans* position)
I: 4.45 Å~4.70 Å = Cl‴···Cl.

The superposed peaks E, G and H can not be clearly separated into the component peaks (corresponding distances), but the corresponding distances of the better models resulting from the selection of intensity curves are fairly consistent with those in the radial distribution curve. That is, two rotationally stable positions of O″···Cl atom pairs are probable $\alpha = 60°$–$75°$ and $\beta = 165°$–$180°$. The corresponding O″···Cl, and C″···Cl distances in these cases are shown under the corresponding peaks G and H by small rectangles whose respective widths show the allowances according to the slight variations of bond distances and angles (see Table I). The existence of a peak of 4.45 Å–4.70 Å corresponding to the Cl‴···Cl distance also seems to show adequately the relative position of the two Cl atoms (see column 11 in Table I).

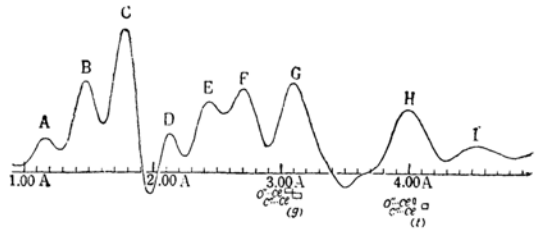


Fig. 3. Radial distribution curve for dichlorohydrin molecule.

Under the curves, the O″...Cl and C″... Cl interatomic distances corresponding to the relative positions in the *gauche* (g) and the *trans* (t) forms respectively are shown with small squares.

$O''\cdots Cl_g$ 3.04~3.09 (Å)
$C''\cdots Cl_g$ 3.09~3.16 (Å)
$O''\cdots Cl_t$ 4.03~4.05 (Å)
$C'\cdots Cl_t$ 4.10~4.15 (Å)

In considering the conclusions in the previous report on ethylene chlorohydrin, that is, the values C–Cl = 1.77 Å, C–O = 1.45 Å, ∠CCC = 109.5° and ∠CCCl = 112° with the assumed C–C = 1.54 Å, the model of dichlorohydrin molecule having the rotational angles $\alpha = 75°$ and $\beta = 180°$ is reasonable (cf. curve N).

b) Ethylene Cyanohydrin.—In constructing molecular models, the following parameters are assumed (i), and varied in the ranges (ii):

(i) C–O = 1.45 Å, C–H = 1.10 Å ($Z_H = 1.2$), C≡N = 1.16 Å[9] and ∠CCO = 109.5°,
(ii) C_1–C_2 = 1.52 Å–1.54 Å, C_2–C_3 = 1.42 Å–1.54 Å and $\angle C_1C_2C_3 = 109.5°$–112°.

The list of models with molecular parameters is shown in Table II, and corresponding theoretical intensity curves in Fig. 4.

Regarding the relative position of –C≡N and –OH radicals, representated by the rotational angle θ, the models are classified into three groups, the *trans* group ($\theta = 180°$, curves from A to E), the *gauche* group ($\theta = 60°$, curves from F to H) and the *cis* group ($\theta = 0°$, curves I and J).

In comparing the intensity relations and *q-values* of maxima and minima of the visual and theoretical intensity curves, the better models are selected by means of the following view-points of analysis;

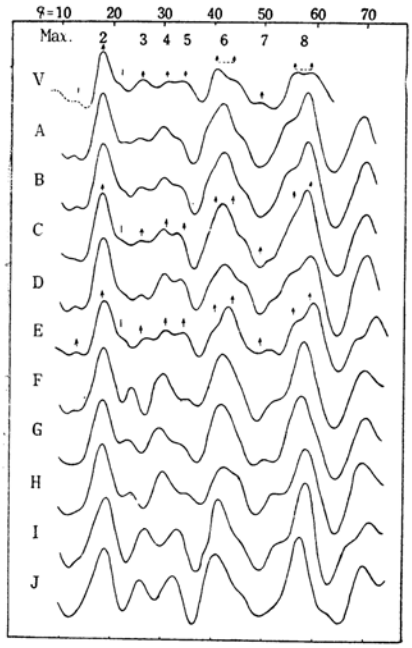


Fig. 4. Visual (V) and theoretical intensity curve for ethylene cyanohydrin molecule.

(1) The *trans*-, *gauche*- and *cis*-forms change clearly in the features of intensity relations as shown in Fig. 4. That is, the maxima 2 and 6 remain almost unchanged throughout the curves; the variation of intensity between maxima 3 and 5 is relatively small in the curves of the *trans*-group (A to E). For the *gauche* group (F to H), both maximum 3 and minimum 4′ shift inward and maximum 4 becomes higher; however, these features do not coincide with those of the visual curve. In the range of $20<q<40$ in the curves I and J (the *cis* group), the simply sinusoidal features differ distinctly from the visual one. The characteristic features of the visual curve are a very low shelf ($q\approx21.8$) accompanying maximum 2 and a slowly-varying intensity between maxima 3, 4 and 5 (i.e. (a) slightly separated low maximum 3 and (b) adjacent maxima 4 and 5 near each other having almost equal heights). These features seem to coincide fairly well with those of the curves in the *trans* group, especially with those of curves E (see later).

(2) From the analysis of the radial distribution curve as shown later, the molecule could be regarded as belonging to the *trans* group, and the C_1–C_2 and C_2–C_3 distances and $\angle C_1C_2C_3$ angles are examined on this assumption.

The C_2–C_3 distance nearest to the triple bond of C≡N can be considered to be short, and the variations of C_2–C_3 distance are compared with one another as: C_2–C_3=1.50 Å (curve B and C), 1.46 Å (curve D) and 1.42 Å (curve E). The case of the angle $\angle C_1C_2C_3=112°$ as shown in the curve C (cf. curve G in the *gauche* form and curve J in the *cis* form having $\angle C_1C_2C_3=112°$) is also compared. In each case, the intensity relation of maxima from 3 to 5 slightly changes, and the heights of maxima 4 and 5 are nearly equal in the visual curve. The curves B, C and D seem comparatively good. The intensity relation of curve E seems the best, although the maxima of curve E shift slightly outward from those of the visual curve in the entire q-range. In spite of the intensity relation of maxima from 3 to 5 being comparatively diffused, it can be safely said, though not conclusively, that the C_2–C_3 distance is slightly shorter than 1.54 Å.

(3) A somewhat obscure and diffuse experimental intensity curve of ethylene cyanohydrin has been obtained up to $q\approx60$, because the sample is a viscous and less volatile liquid having high boiling temperature. Despite this, a radial distribution curve, curve RD1 has been computed with some uncertainty as shown in Fig. 5. From the curve, the corresponding atom pairs and distances between each peak are analyzed as follows:

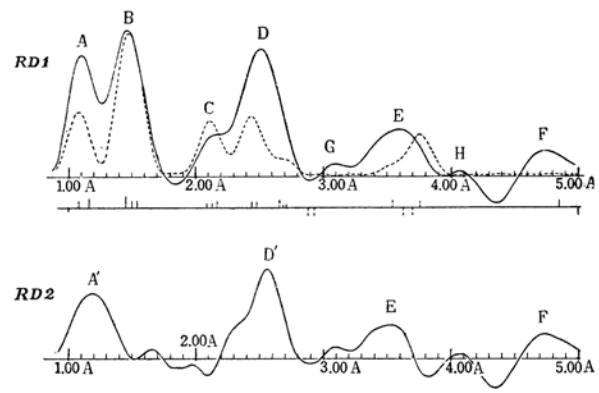


Fig. 5. Radial Distribution curves for ethylene cyanohydrin molecule.
*RD*1, total radial distribution curve. *RD*2, the curve which shows the residual curve produced by the subtraction of the area under the hypothetical partial *RD* curve (as shown by the dotted curve) from the area under the *RD*1 curve.

A: C-H, C≡N,
B: C_1-C_2, C_2-C_3 C-O,
C: C′···H, O′···H,
D: C′···O (≈2.40 Å), C′···C (2.43 Å∼2.55 Å),
O″···H (≈2.70 Å), C′···N (2.66 Å∼2.70 Å),
E: C″···N (3.48 Å∼3.55 Å),
C″...O_{trans} (3.30 Å∼3.79 Å),
F: O‴...N_{trans} (4.83 Å∼4.88 Å).

Each of these analyzed values seems to agree fairly well with each corresponding parameter of the better models. In particular, the *trans*-form seems acceptable as regards the rotational equilibrium position around the C_1-C_2 bond. That is, the peak F (4.70 Å-4.80 Å) does not appear in the cases other than the *trans* form: for example, if the *gauche* formexists, the peak corresponding to O″···O_{gauche}≈2.85 Å∼2.95 Å will appear, but not in RD1. It is not clear, however, whether or not the two rotational isomers may coexist. The distances other than O‴···N_{trans} (peak F) cannot be determined separately from the curve RD1, since the other peaks appear to be the combinations of two or more peaks. From consideration of the intensity curves, the dotted curve which is the hypothetical radial distribution curve of the following eight distances on RD1, is computed;

C-H=1.08 Å, C-O=1.45 Å, C_1-C_2=1.54 Å*,
C′···H=2.17 Å**, C′···O=2.44 Å**,
C″···O_{trans}=3.76 Å**, O″···H_{gauche}=2.69 Å**,
N′···H=3.55 Å**.

In consequence of the subtraction of the area under the dotted curve from that of RD1, the peaks other than those corresponding to eight distances mentioned above appear in the curve RD2.

The new distribution curve RD2 is analyzed with some uncertainty as follows:

A′: The peaks corresponding to the distances C≡N and C_2-C_3 should appear, but could hardly be separated.
D′: 2.56 Å=C_2′···N,
E′: 3.45 Å∼3.60 Å=C″···N,
from this value the angle ∠$C_1C_2C_3$ could not be decided conclusively.

The intensity curve E, which is computed in consideration of the results of radial distribution curve, seems to be the most acceptable one, except the shape of maximum 6 and the slight disagreements of all *q-values*. The structure of ethylene cyanohydrin could not be determined more fully, because only insufficient diffracted patterns were obtained.

Results and Discussions

1) α,γ-Dichlorohydrin.—From the intensity and radial distribution curves, the following results are obtained:

C-Cl=1.76 Å-1.80 Å, ∠CCC=109.5°±1.5°,
∠CCCl=111°±1.5°,
α=70°±10°, β=180°±10°.

The results of α, γ-dichlorohydrin seem sufficiently acceptable in comparison with those of ethylene chlorohydrin.

One of the two O″···Cl atom pairs is in the *gauche* position and the other *trans* at room temperature, because probably intramolecular hydrogen bond can only be formed in one or the other set of O″···Cl atom pairs.

2) Ethylene Cyanohydrin.—
C_2-C_3=(1.48 Å±0.04 Å)<C_1-C_2
θ=180° (The stable form of rotation about C_1-C_2 bond is of *trans*.)

Upon consideration of the present results, the C_2-C_3 bond neighboring the triple bond C≡N seems to be comparatively short. In the series of bonds -C_2-C_3≡N, the N atom is capable of becoming a weak "proton-acceptor", while the C_3 atom does not have this capacity. However, it is probably difficult to form the intramolecular hydrogen bond O-H···N in this molecule because of the longer distance of the O···N atom pair and of the repulsive force between the O···C_3 atom pair in the *cis* form (i.e. O···N_{cis}=3.20Å and O···$C_{3,cis}$=2.60Å). Consequently, the molecule exists almost in the *trans* form in the gaseous state, and the coexistence of another isomer forming the intramolecular hydrogen bond can not be confirmed.

Summary of Results

The molecular structures of α, γ-dichlorohydrin and ethylene cyanohydrin in the gaseous state were investigated by a visual electron diffraction method. The results obtained from the analyses of intensity curves and radial distribution curves are as follows:

α, γ-Dichlorohydrin (1, 3-dichloropropanol (2))

Assumption: C-C=1.54 Å, C-O=1.45 Å, and C-H=1.10 Å and ∠CCH=∠CCO=109.5°.
Results: C-Cl=1.78 Å±0.02 Å, ∠CCC=109.5°±1.5° and ∠CCCl=111°±1.5°.
Stable rotational position: α=70°±10°, β=180°±10°.

Ethylene Cyanohydrin

Assumption: C-H=1.10 Å, C_1-C_2=1.52 Å-1.54 Å, C≡N=1.16 Å, ∠CCH=10.95°, ∠$C_1C_2C_3$=109.5°-112°
Results: C_2-C_3=(1.48 Å±0.04 Å)<C_1-C_2.
Stable rotational position: θ=180° (*trans* form).

* In order to obtain the peak corresponding to C_2∼C_3, the value of C_1−C_2 is assumed.
** These values should be varied functionally with the angle ∠$C_1C_2C_3$, but the values are assumed in the first approximation.

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