Molecular Structure Investigations by Electron Diffraction Method. III. The Molecular Structure of Ethylene Fluorohydrin

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(Received December 7, 1955)

Introduction

In regard to the molecular structure of ethylene chlorohydrin, many investigations were made as mentioned in the previous report¹⁾. From electron diffraction studies of this molecule, it was concluded that the structure having the rotational angle $\varphi=75°$ about the C–C bond is predominant at room temperature.

A few structural investigations of ethylene fluorohydrin molecule have been made²⁾. In this report the structure has been investigated in relation to the rotationally stable form of this molecule including the problem of intramolecular hydrogen bonding. Moreover, the problem of the bond length C–F of fluorine-substituted compounds is very interesting, and this problem has also been taken into consideration.

Experimental Procedures

(1) **Sample.**—The ethylene fluorohydrin has been synthesized according to F. W. Hoffmann's method³⁾.

122.5 g. potassium fluoride (previously dried by heating and powdered) is mixed with 112 g. dried ethylene glycol and 45.5 g. diethylene glycol in a flask, and then heated with continuous stirring at a temperature about 175°–185°C, while 114.5 g. ethylene chlorohydrin is being gradually dropped into the flask. The addition of the chlorohydrin takes about 2.5 hours. Gaseous evaporate is distilled out through a rectifying column filled with small glass balls, the temperature at the top of the column being held constant at 100°C.

Finally, air is blown into the reaction product in the flask, and the distillate is completely distilled. Sodium fluoride is added to the distillate, and the ethylene fluorohydrin thus produced is collected by distillation at a temperature between 95°–105°C (boiling point). As traces of water mixed in the fluorohydrin cannot be removed by distillation, the product is left with dehydrated Glauber's salt (sodium sulfate anhydride) for many days for dehydration before final distillation.

(2) **Photograph of Diffracted Pattern.**—The apparatus of electron diffraction is the same as that described in the previous report⁵⁾, and a horizontal type camera having a camera length of 130 mm. was also used.

Generally the halos of this pattern are lacking in sharpness and are comparatively diffused. Eight diffracted halos have been measured

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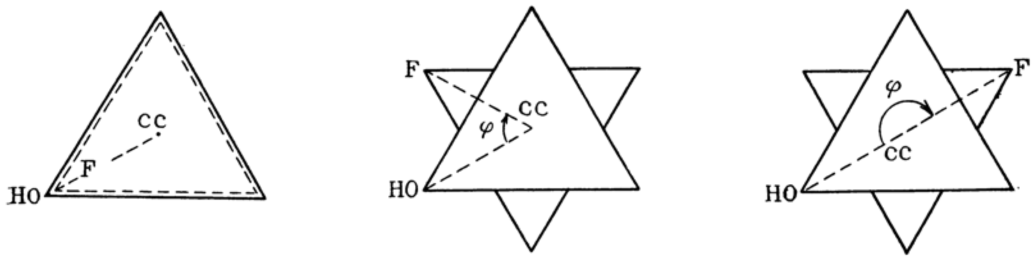
2) For Example, H.D. Cowan, M. Herman, et al., "Raman spectra of single fluorine compounds", *Ind. chim. belge.*, **16**, 86 (1951).

3) F.W. Hoffmann, *J. Am. Chem. Soc.*, **70**, 2596 (1948).

4) M. Kimura, *J. Chem. Soc. Japan* (in Japanese), **71**, 18 (1950).

5) T. Yuzawa and M. Yamaha, This Bulletin, **26**, 414 (1953).



Cis Form
$\varphi=0°$

Gauche Form
$\varphi=60°$

Trans Form
$\varphi=180°$

Fig. 1. Schematic models showing the rotational angle φ about the C–C bond for ethylene fluorohydrin molecule.

TABLE I

THE MOLECULAR MODELS AND CORRESPONDING ASSUMED MOLECULAR CONSTANTS (cf. Fig. 2)

Groups	Models	C–O (Å)	C–F (Å)	∠CCO°	∠CCF°	O″···F (Å)
Trans	T1	1.43	1.36	109.5	107	3.58
	T2	1.48	1.40	109.5	112	3.71
Gauche	G3	1.43	1.36	109.5	107	2.75
	G4	1.45	1.36	108	109.5	2.75 (C–C=1.50
	G5	1.45	1.36	109.5	109.5	2.77 (C–C=1.50
	G6	1.45	1.33	109.5	109.5	2.80
	G7	1.48	1.40	109.5	107	2.80
Form of $\varphi=30°$	8	1.43	1.36	109.5	107	
Cis	C9	1.43	1.36	109.5	107	2.42
	C10	1.48	1.40	109.5	112	2.56

visually, up to the limit of the range $q<75$ from about 20 photographed plates.

The measured *q-values* of the maxima and minima are shown in Table III, and the visual intensity curve is shown at the top of Fig. 2.

Molecular Models and Theoretical Curves

(1) The theoretical intensity curves for the assumed molecular models have been calculated by the use of the well-known Pauling-Schomaker formula:

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

where Z_i is the atomic number of the atom i. Z_H is assumed to 1.25.

$q=10\,s/\pi$, $s=(4\pi\sin\theta/2)/\lambda$, θ: the scattering angle,

r_{ij}: the distance between the ith and jth atoms,

λ: the wave length of the electron beam used,

b'_{ij}: the temperature factor for the atom pair i–j.

(2) The assumed molecular models corresponding to the theoretical intensity curves in Figs. 2 and 3 are tabulated in Tables I and II. In constructing the models, the bond distance C–H=1.09 Å and the angle ∠CCH=109.5° are assumed.

The models are divided into several groups according to the rotational equilibrium positions about the C–C bond, that is, the *trans, gauche*, the form of $\varphi=30°$ and *cis* groups (see Fig. 1). Secondly, in each group, the bond length C–O varies from 1.43 to 1.48 Å, C–F from 1.33 to 1.40 Å, and ∠CCF from 107° to 112°. Thirdly, in the case of the *gauche* group, the angle φ varies from 30° to 75°. In this case, the other parameters are assumed to be C–C=1.54, C–O=1.43, C–F=1.36 Å and ∠CCF=∠CCO=109.5°.

The value b_{ij}'s used for each atom-pair are shown in Table VI.

TABLE II

THE MOLECULAR MODELS AND CORRESPONDING ASSUMED MOLECULAR CONSTANTS IN REGARD TO THE VARIATION OF ANGLE φ
C–C=1.54 Å, C–O=1.43 Å, C–F=1.36 Å and ∠CCF=∠CCO=109.5 are assumed constantly

Models	$\varphi°$	O″...F(Å)
A	75	2.94
B	68	2.88
C	60	2.80
D	45	2.67
E	38	2.62
F	30	2.56

TABLE III

OBSERVED q-VALUES AND CALCULATED q/q_{obs}. VALUES FOR THE BETTER MOLECULAR MODELS

Max.	Min.	q_{obs}	q/q_{obs} G4	G5	B	C
1		(10.87)	(0.892)	—	—	—
	2′	(14.37)	(0.905)	—	(0.891)	(0.898)
2		18.99	0.995	1.006	0.995	0.979
	3′	24.80	1.008	0.980	0.996	1.008
3		29.39	1.034	1.028	1.014	1.044
	4′	33.39	(1.045)	—	0.994	—
4		36.09	1.006	—	0.975	—
	5′	39.56	1.001	0.996	0.998	1.001
5		44.17	0.998	0.994	0.988	1.003
	6′	49.82	0.974	0.965	0.959	0.976
6		52.88	0.970	0.953	0.957	0.978
	7′	56.18	0.970	0.961	0.968	0.981
7		60.19	0.990	0.985	0.995	0.995
	8′	65.58	1.016	1.016	1.019	0.988
8		70.20	1.019	1.010	1.004	0.957
Mean Average:			0.998_4	0.990_4	0.989_4	0.991_8
Mean sq. deviation:			0.019	0.023	0.019	0.022

(3) The radial distribution curve

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

is calculated by using the best visual intensity curve V for the function $I(q)$, where the value a is determined to be $\exp(-aq^2_{\max})=0.1$, $q_{\max}$ being about 75.

Comparisons of the Intensity Curves and the Selection of the Best Model

From the comparison of the visual and theoretical intensity curves as shown in Fig. 2 and from the analysis of the radical distribution curve as shown in Fig. 4, the characteristic features for the selection of the best model are specified as follows:

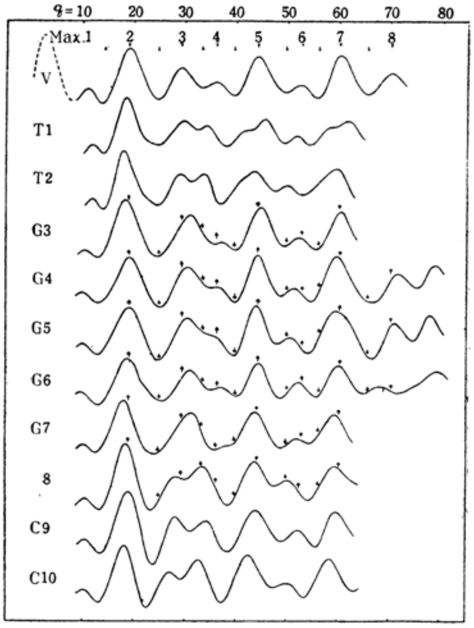


Fig. 2. Visual (V) and theoretical intensity curves for ethylene fluorohydrin molecule. (cf. Table I).

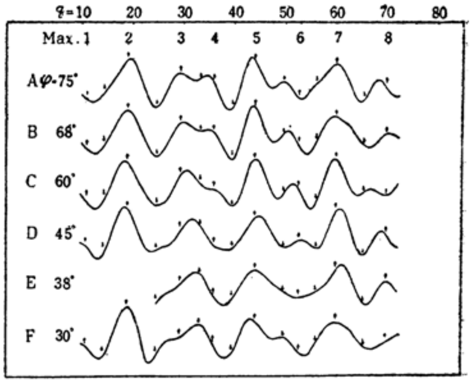


Fig. 3. Theoretical intensity curves showing the variations of models according to the changes of angle φ. (cf. Table II).

TABLE IV

THE DISTANCE O″…F *gauche* IN RELATION TO OTHER MOLECULAR CONSTANTS

C–C (Å)	C–O (Å)	C–F (Å)	∠CCO°	∠CCF°	O″…F (Å)	Models
1.54	1.43	1.36	109.5	109.5	2.75	G3
1.50	1.45	1.36	108	109.5	2.75	G4
1.54	1.43	1.40	109.5	107	2.77	
1.50	1.45	1.36	109.5	109.5	2.77	G5
1.54	1.48	1.36	109.5	107	2.78	
1.54	1.43	1.36	109.5	109.5	2.80	C
1.54	1.45	1.33	109.5	109.5	2.80	G6
1.54	1.48	1.40	109.5	107	2.80	G7
1.54	1.43	1.36	109.5	112	2.84	
1.54	1.43	1.40	109.5	112	2.87	
1.54	1.48	1.36	109.5	112	2.87	
1.54	1.48	1.40	109.5	112	2.89	

TABLE V

THE LIST OF MOLECULAR CONSTANTS OF FLUORINE-SUBSTITUTED COMPOUNDS

Molecules	C–C (Å)	C–F (Å)	C–Cl (Å)	Other Parameters	References
CCl_3F		1.40			6), 7)
$CHCl_2F$		1.40	1.76		6)
CCl_2F_2		1.35	1.74	∠FCF=108°48′	6), 7)
CH_3F		1.332			8)
CHF_2		1.39 (1.384)			9)
$CClF_3$		1.328	1.740	∠FCF=108°, ∠FCF=110°	10)
CF_3–COOH		1.36			11)
CH_3–CCl_2F		1.40	1.78	∠CCF=109.5°, ∠CCCl=111°	12)
CH_3–$CClF_2$		1.37	1.77	∠CCF=∠CCCl=111°, ∠FCF=∠FCCl=108°	12)
CH_3–COF		1.41			13)
CH_3–CF_3	1.45	1.33		∠FCF=108.5°	14)
	1.53	1.36		∠CCF=112°, ∠FCF=107°	12)
	1.54	1.33			15)
CF_3–CF_3	1.45 (±0.06)				16)
($CClF_2$–$CClF_2$)	1.45 (ass.)	1.33	1.74		17)

(1) Comparison of each group corresponding to the *trans*, *gauche* and *cis* forms of molecular models.

a) The curves corresponding to the *trans* and *cis* groups are comparatively similar in shape, but the *q-values* of each maximum or minimum are different from one another. Further, the intensity relations of max. 3 and max. 4 differ slightly from one another, and also the shapes of max. 5 and max. 7 are broad with the shelf-like feature in the *trans* form.

b) Max. 3 and the accompanying shelf-like max. 4 are characteristic of the *gauche* group. These features are slightly different from those of the other groups.

So far as the considerations of these features, as compared with those of the visual curve, are concerned, the curves of the *gauche* group appear to be in best agreement (see Fig. 2, curves G4 and G5, and section (4)).

(2) In the *gauche* form, the variation of the O″···F distance, depending upon the variations of the parameters C–O, C–F and ∠CCF, is listed in Table IV, (not all of the corresponding curves are shown in Figs. 2 and 3).

The variation of the intensity relation of each curve is not so clear as to determine each allowable range of the respective parameters C–O, C–F and ∠CCF independently. However, from the analysis of the radial distribution curve, the distance O″···F seems to be in the vicinity of the value r=2.81 Å (see (4)). The intensity curves for which O″···F is about 2.81 Å are generally satisfactory.

The curve G6, having a smaller distance C–F=1.33 Å, is hardly satisfactory, because the *q-values* of max. 3, max. 4 and max. 8 clearly show disagreement with those of the visual curve.

(3) When the rotational angle φ is varied from 30° to 75°, the smaller the angle φ becomes, the more max. 3 shifts toward larger *q-values*, accompanied by the disappearance of the shelf-like max. 4 and the later appearance of a small shelf-like maximum at about the position of max. 3 in the visual curve.

Up to a point, the larger the angle φ becomes, the more the intensity relations of all the maxima and minima agree with that of the measured visual curve; but when φ= 75°, the features of max. 3, max. 4 and max. 7 become similar to those of the *trans* form, that is, max. 4 approaches max. 3, max. 7 becomes broader with a small shelf, and the *q-values* of each maximum shift slightly from those of the visual curve.

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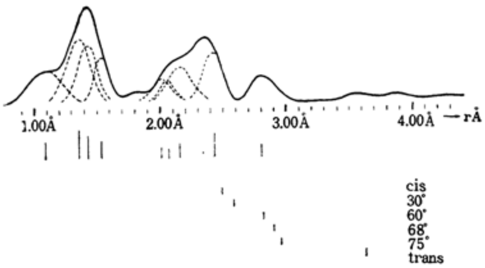

Fig. 4. Radial distribution curve for ethylene fluorohydrin molecule.

Under the curve, the interatomic distance corresponding to each peak is shown by the short line.

O″···F distance which corresponds to the variation of rotational angle φ from 0° (*cis*) to 180° (*trans*) is also shown in due order under the corresponding position of the curve. (cf. Tables I and II).

The model which has the rotational angle about $\varphi=60°\text{–}70°$ (see Fig. 3, B and C) seems to be the best.

(4) When attention is paid to the radial distribution curve (Fig. 4), two broad peaks appear in the range of $r<2.6$ Å, each of the peaks being the superposition of several interatomic distances: that is, one corresponds to the peaks of the distances C–F, C–O and C–C, and the other to those of F′···H, O′···H and C′...O, etc. However, all the broad peaks cannot be analyzed accurately as peaks of respective component distances.

For the present purpose, particular peaks corresponding to the assumed interatomic distances (for example, C–H, C–F, C–O, C–C, F′···H, O′···H, C′···O, etc.) are indicated by dotted lines on the distribution curve (Fig. 4).

It is expected that the comparatively large peak corresponding to the distance C′···O which is related to the angle ∠CCO and the length C–C appears at the point about $r=$ 2.4 Å. On the distribution curve, there seems to be a corresponding peak at the point $r=$ 2.38 Å. The distance 2.38 Å seems to be slightly smaller than 2.44 Å, the normal distance of C′···O.

The shortening of this distance can be interpreted in two ways: the angle ∠CCO may be slightly smaller than 109.5° (nearly 108°), or the distance C–C may be about 1.50 Å*, in both cases the distance C–O being assumed to be 1.45 Å.

The intensity curves G4 and G5 correspond to the models which have the distance C–C= 1.50 Å. G4, having ∠CCO=108°, and G5, having ∠CCO=109.5°, coincide better with the visual curve than the others in the *gauche* group.

(5) On the radial distribution curve, the peak corresponding to the distance O″···F appears distinctly at about $r=2.81$ Å, and this distance agrees rather well with the O″···F distance of the *gauche* form.

In the cases of C–C=1.50 Å mentioned above (G4, G5), the O″···F distance seems to be slightly smaller than the value 2.81 Å. As a result, the cases of $\varphi>60°$, that is, those which allow slightly longer O″···F, are considered. Upon comparing the curves of the group of the *gauche* form with B and C, the curves B and C are seen to coincide fairly well with the visual one with respect to the intensity relations and *q-values*.

(6) No peak corresponding to the *trans* distance of O″···F appears in the presumable r range in the radial distribution curve, and therefore the *trans* and *gauche* isomers of this molecule hardly seem to co-exist.

(7) In the curves A to F in Fig. 3, the effects of temperature factors are taken into account (as tabulated in Table VI). However, since the characteristic features of these curves appear to change very little, these factors are not considered in further details.

Discussion and Summary of Results

From the preceding considerations, the intensity curves G4, G5, B and C seem to be regarded as satisfactory, and the final results of the molecular structure of ethylene fluorohydrin have been obtained as follows:

C–O=1.45 Å±0.02 Å O″···F=2.82 Å±0.03 Å,
C–C=1.50 Å∼1.55 Å ∠CCF=109°±2°,
C–F=1.35 Å∼1.40 Å ∠CCO=109.5°±2°.

Through many other investigations, that is, the results of ethylene chlorohydrin¹⁾, ethyl alcohol⁴⁾, and isopropyl alcohol⁵⁾, the same conclusion has been reached as regards the bond distance C–O=1.45 Å.

According to many structural investigations of fluorine-substituted compounds, the slightly shorter distances C–C<1.54 Å and C–F= 1.36 Å∼1.40 Å seem to be satisfactory (see Table V).

TABLE VI

APPROXIMATE TEMPERATURE FACTORS b'_{ij} USED IN CALCULATIONS

$b'_{ij}=0$ for C–C,
$b'_{ij}=-0.00016$ for C–O, C–F, C′···O, C′···F and C″···F,
$b'_{ij}=-0.00030$ for C′···H, O′···H, F′···H, O″···H and F″···H.

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* In the investigations flourine-substituted compounds, it has often been observed tha. the distance c-c is slightly smaller than the normal covalent distance 1.54Å (see Table V).

In regard to paraffines in which two or more hydrogen atoms have been substituted by fluorine atoms, a smaller value of distance C–F>1.35 Å has often been found, but the distance C–F<1.35 Å seems adequate in the case of this molecule.

In the case of ethylene chlorohydrin, it was concluded that the *gauche* and the *trans* forms co-exist, but a similar conclusion can not be reached in the present compound. From the analysis of the radial distribution curve, it is concluded that there is almost certainly one form of this molecule at room temperature. That is, the ethylene fluorohydrin molecule is of the *gauche* form ($\varphi=60°–70°$), and is considered to form the intramolecular hydrogen bond. This is a reasonable interpretation by virtue of the fact that hydrogen bonding of the type O–H···F seems to be stronger than that of the type O–H···Cl[18]: even in the case of ethylene chlorohydrin, the *gauche* from seems to be predominant at room temperature.

The author wishes to express his deep gratitude to the late Professor H. Oosaka of this University and to Professor Y. Morino of Tokyo University, for their kind advice throughout this work.

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