The Molecular Structure of 1, 2-Difluoro-1, 1, 2, 2-tetrachloroethane

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Introduction

The molecular structure of 1, 2-difluorotetrachloroethane offers two interesting problems. One is concerned with rotational isomerism while the other with the effect of the neighbouring halogen atoms on the C—F and C—Cl bond distances.

The phenomenon of the rotational isomerism in halogenated ethanes has been the subject of a great number of investigations during the past two decades. However, most of these works have been carried out by measuring the change of dipole moments or infrared absorptions with temperature compared with the results of which measurements by electron diffraction are meagre. Furthermore, the general applicability and the merits of various potential functions[1,2] that have recently been proposed cannot be criticized until comprehensive data on the structure of related molecules are available. Therefore it is desirable to carry out a study by electron diffraction side by side with studies by spectroscopy and dipole moment measurement.

Having such points in mind, the present writers have undertaken the herein described work in order to determine the molecular structure and the energy difference between two isomers by means of electron diffraction.

Experimental

Sample

The sample was prepared by the fluorination of hexachloroethane with SbF_3 in the presence of $SbCl_5$ as a catalyst. The product distilled at 92.5°C. The purity of this sample was tested with an infrared absorption spectrum. It was confirmed that the amount of CCl_3—CF_2Cl, which could not be removed by fractionation, was less than about one per cent. Hence the amount was not great enough to affect the electron diffraction pattern.

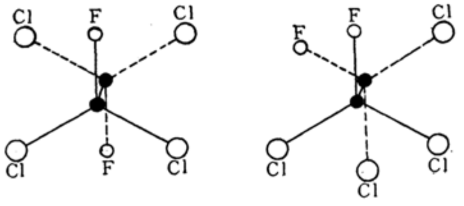
Procedure

The diffraction patterns of 40 KV. electrons were obtained at a temperature of about 15°C using a rotating sector apparatus, which will be described in detail elsewhere. Two camera distances of 28 cm. and 12 cm. were used with an s^2 sector. The photographic density was measured up to $q=90$ by a recording microphotometer. In this measurment, the photographic plate was rotated rapidly about the center of the diffraction pattern in order to smooth out the inevitable irregularities. The traces thus obtained were measured by a coordinate comparator as a function of q. A procedure[3] similar to that employed by J. Karle was used for deriving an experimental intensity curve from the microphotometer record.

The experimental intensity curve, I_m, was obtained from the curve of the total scattered intensity, I_t, by drawing a smooth background, I_b, then

$$I_m=(I_t/I_b)-1. \tag{1}$$

The curve A shown in Fig. 4 is I_m multiplied by q, where the dotted portion is drawn by use of a theoretical intensity curve described below.



trans form *gauche* form

Fig. 1. Stable configurations of $CFCl_2$-$CFCl_2$.

Analysis

The radial distribution curve shown in Fig. 2 was calculated by the following equation:

$$f(r)=\sum_{q=0}^{q_{\max}} qI_m \exp(-aq^2)\sin(\pi qr/10), \tag{2}$$

where $a=0.00288$.

The curve has maxima at 1.38, 1.76, 2.5—3.3, 3.92 and 4.33Å. The first two peaks at 1.38 and 1.76 Å correspond to C—F and C—Cl bond distances, respectively. The peak at 2.5—3.3 Å is due to various non-bonded distances, while that at 4.33 Å to the *trans* Cl···Cl distance. The peak at 3.92 Å corresponds to the *trans* F···Cl distance, which is characteristic of *gauche* configuration (see Fig. 1). This peak evidently shows the existence of the *gauche* form. If only the *gauche* form exists, the ratio of the area of the peak at 4.33 Å to that at 3.92 Å must have the value of 0.86. The fact that the observed ratio has the value of 2.43, indicates that the *trans* form, having no *trans* F···Cl distance, coexists with the *gauche* form (see Fig. 1). The ratio of the two forms, N_t/N_g, can be calculated from the areas of the two peaks noted above by means of the following formula:

$$\frac{N_t}{N_g}=\frac{Z_F\, r_{Cl\cdots Cl} A_{Cl\cdots Cl}}{Z_{Cl} r_{F\cdots Cl} A_{F\cdots Cl}}-\frac{1}{2}, \tag{3}$$

where $A_{Cl\cdots Cl}$ and $A_{F\cdots Cl}$ are the areas of the peaks and $r_{Cl\cdots Cl}$ and $r_{F\cdots Cl}$ are the equilibrium distances for the *trans* Cl···Cl and *trans* F···Cl, respectively. The application of this formula leads to a value of 52 per cent. for the amount of the *gauche* form.

In the calculation of the radial distribution curve, in place of the intensity curve below $q=17$ the theoretical intensity was substituted. The ratio of the areas was affected by the value of the abundance ratio of the two isomers assumed in the calculation of the theoretical part of the intensity. Therefore, the method of successive approximation was taken. If the theoretical part is calculated for 100 per cent. *gauche* form, formula 3 above leads to a value of 78 per cent. for the amount of the *gauche* form. Next, assuming the amount of the *gauche* form to be equal to 78 per cent. a value of 71 per cent. was obtained. The successive approximation being carried out as given above, a self-consistent value of 52 per cent. was obtained. This value was scarcely affected by the values of molecular parameters assumed in the calculation. The radial distribution curve shown in Fig. 2 was

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1) W. D. Gwinn and K. S. Pitzer, *J. Chem. Phys.*, **16**, 303 (1948).

2) H. J. Bernstein, ibid., **17**, 262 (1949).

3) I. L. Karle and J. Karle, ibid., **17**, 1052 (1949) ; **18**, 957 (1950).

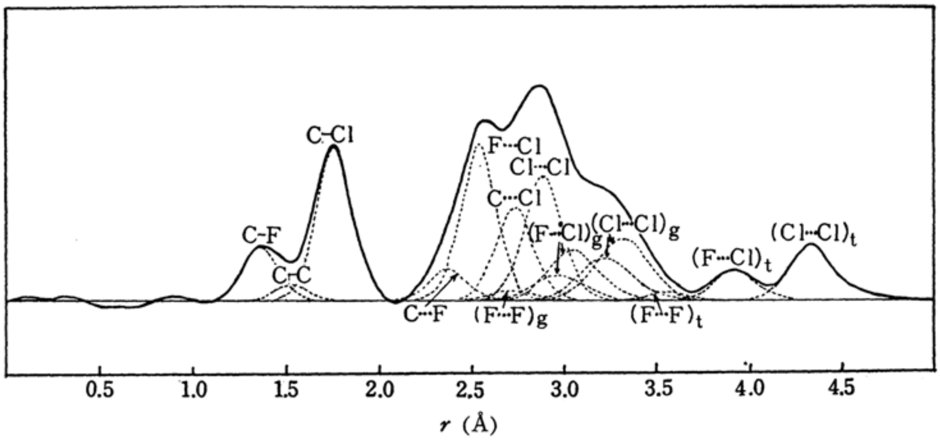

Fig. 2. Radial distribution curve of $CFCl_2—CFCl_2$.

obtained by the procedure described above using the values of molecular parameters listed in Table III.

The part from 2.5 to 3.3 Å of the radial distribution curve corresponds to the superposition of the contributions of 10 interatomic distances in the *trans* as well as in the *gauche* form. This part of the radial distribution curve calculated as the sum of Gaussian curves, each corresponding to the contribution of an interatomic distance, was in good agreement with the experimental curve, when the amount of the *gauche* form was assumed to be about 50 per cent. The assumed values of the mean amplitudes used in this calculation are listed in Table I. The dotted curves shown in Fig. 2 depict the contributions of various interatomic distances. Although the assumed values were used for the mean amplitudes, the result from this part of the radial distribution curve serves to confirm the percentage of the *gauche* form derived from the ratio of the peak areas at 4.33 and 3.92 Å.

The shelf at 3.2 Å corresponds to the *gauche* Cl···Cl distance in the *gauche* form*. Therefore, from this portion of the radial distribution curve, the value of 55—63° was obtained for the azimuthal angle of F—C—C—F of the *gauche* form.

The analysis of the over-all feature of the radial distribution curve gave the values listed in Table III for the interatomic distances and the valency angles. Other items of information obtained from the radial distribution curve are the values of the mean amplitudes of the bonded C—F, bonded C—Cl, *trans* F···Cl, and *trans* Cl···Cl distances. The mean amplitudes of other distances could not be determined because of the superposition of many interatomic distances in the radial distribution curve. If the observed peaks are made to fit Gaussian curves, the values listed in Table I are obtained for the mean amplitudes of these distances, which agree with the values calculated by Morino et al.[4]

TABLE I

OBSERVED AND ASSUMED MEAN AMPLITUDES IN Å

Distance	Obs.	Calcd.	Distance	Obs.	Calcd.
C—F	0.064	0.045	$(F\cdots F)_g$		0.114
C—C		0.050	$(F\cdots Cl)_g$		0.120
C—Cl	0.062	0.050	$(Cl\cdots Cl)_g$		0.125
C···F		0.059	$(F\cdots F)_t$		0.061
F···Cl		0.065	$(F\cdots Cl)_t$	0.070	0.070
C···Cl		0.073	$(Cl\cdots Cl)_t$	0.081	0.074
Cl···Cl		0.070			

The theoretical intensity curves were calculated by use of the following equation:

$$qI(q)=\sum\sum_{i>j}\frac{Z_iZ_j}{r_{ij}}\exp(-b_{ij}q^2)\sin(\pi q r_{ij}/10) \quad .(4)$$

In this equation, notations have their usual significances. The constant b_{ij} was calculated from the mean amplitudes listed in Table I. Though the majority of these values are calculated by Morino et al.[4] from spectroscopic data, the values for the non-bonded F···Cl and the *trans* F···Cl distances were assumed appropriately from other data. The values for the *gauche* F···F and the *gauche* Cl···Cl distances were taken from Karle's experimental data on C_2Cl_6[5] and C_2F_6[6] by ascribing the contribution of the torsional oscillation to the over-all vibration. For the *gauche* F···Cl distance, use was also made of Karle's data.

The curve A in Fig. 3 is of 100 per cent. *trans* form and the curve E of 100 per cent. *gauche* form for the model obtained from the radial distribution curve on the assumption that the structural frame of the molecule does not change with rotation. The curves B, C and D are of the isomeric mixture, in which the amount of the *gauche* form is 30, 50 and 70 per cent. respectively. The curve for the *trans* form as well as the *gauche* does not agree with the experi-

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* The *gauche* Cl······Cl distance of the *trans* form is somewhat smaller than this value.

[4] Y. Morino, K. Kuchitsu, A. Takahashi and K. Maeda, *J. Chem. Phys.*, **21**, 1927 (1953).

[5] D. A. Swick, I. L. Karle and J. Karle, ibid., **22**, 1242 (1954).

[6] D. A. Swick and I. L. Karle, ibid., **23**, 1499 (1955).

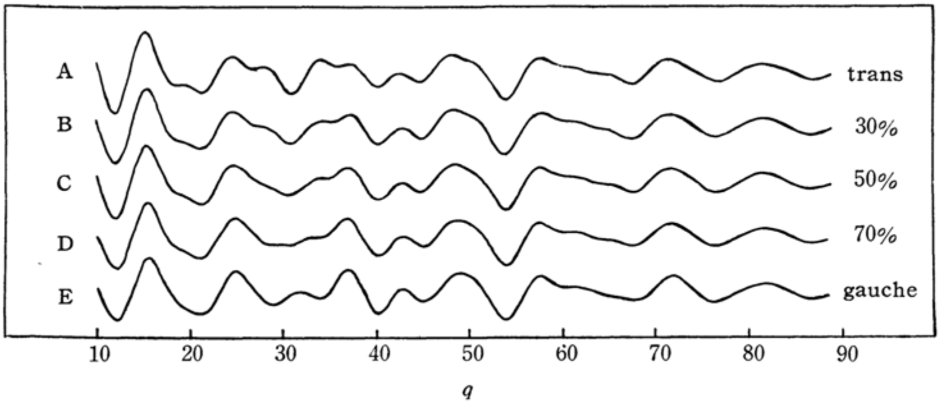

Fig. 3. Theoretical intensity curves of $CFCl_2—CFCl_2$.

TABLE II

MOLECULAR PARAMETERS FOR $CFCl_2—CFCl_2$

Model	C—F	C—C	C—Cl	∠CCCl	∠ClCCl	∠FCCl
B	1.38 Å	1.54 Å	1.76 Å	112°	110°30′	107°30′
C	〃	〃	〃	110°	〃	107°
D	〃	〃	〃	114°	〃	〃
E	〃	〃	〃	112°	109°30′	〃
F	〃	〃	〃	〃	110°30′	〃
G	〃	〃	〃	〃	111°30′	〃
H	〃	〃	〃	〃	110°30′	106°
I	〃	〃	〃	〃	〃	108°
J	〃	〃	1.73	〃	〃	107°
K	〃	〃	1.79	〃	〃	〃
L	1.34	〃	1.76	〃	〃	〃
M	1.42	〃	〃	〃	〃	〃
N	1.38	1.48	〃	〃	〃	〃
O	〃	1.60	〃	〃	〃	〃
P	〃	1.54	〃	〃	〃	〃
Q	〃	〃	〃	〃	〃	〃
R	〃	〃	〃	〃	〃	〃

ment. The curve for the mixture is in satisfactory agreement with the experiment, if the *gauche* form is present in an amount nearly equal to 50 per cent. The result confirms definitely the amount of the *gauche* form already derived from the radial distribution curve.

Moreover, the limits of errors in the percentage of the *gauche* form as well as the values of the interatomic distances, the valency angles, and the azimuthal angle of the *gauche* form were determined by the analysis of 100 theroretical intensity curves for models having a C—F distance ranging from 1.30 to 1.42 Å, a C—Cl distance from 1.73 to 1.79 Å, a C—C distance from 1.45 to 1.60 Å, ∠CCCl from 109°28′ to 115°, ∠ClCCl from 109°28′ to 111°30′ and ∠FCCl from 109°28′ to 105°30′. Some of them are shown in Fig. 3 in order to illustrate the dependence of the relative positions and intensities of maxima and minima upon the parameters. The values of the parameters used are listed in Table II. Curve B in Fig. 4 gives the best model. It reproduces the feature of the experimental curve in a satisfactory manner. The mean value of q/q_0 for the maximum and minimum positions is 1.000 with an average deviation of 0.002.

The variation in the parameter ∠CCCl causes changes mainly in the regions $18<q<23$ and $30<q<40$, that of ∠ClCCl mainly in the region $39<q<47$, that of ∠FCCl mainly in the region $47<q<52$, that of C—Cl mainly in the positions of the maxima and minima, and those of C—F and C—C mainly in the regions $30<q<40$ and $47<q<52$ as shown in curves C, F and D, curves E, F and G, curves H, F and I, curves J, F and K, curves L, F and M, and curves N, F and O, respectively. It was assumed for the sake of comparison that the three *gauche* Cl···Cl distances in the *gauche* form were equal and the amount of the *gauche* form was 50 per cent. in all of the models described above, although the change in the azimuthal angle or the amount of the *gauche* form may improve the agreement with the experimental curve. The changes due to the variation of these two parameters are illustrated in curves P, Q and R of Fig. 4 and curves B, C and D of Fig. 3. The curves P, Q and R depict the theoretical intensity for the models of the azimuthal

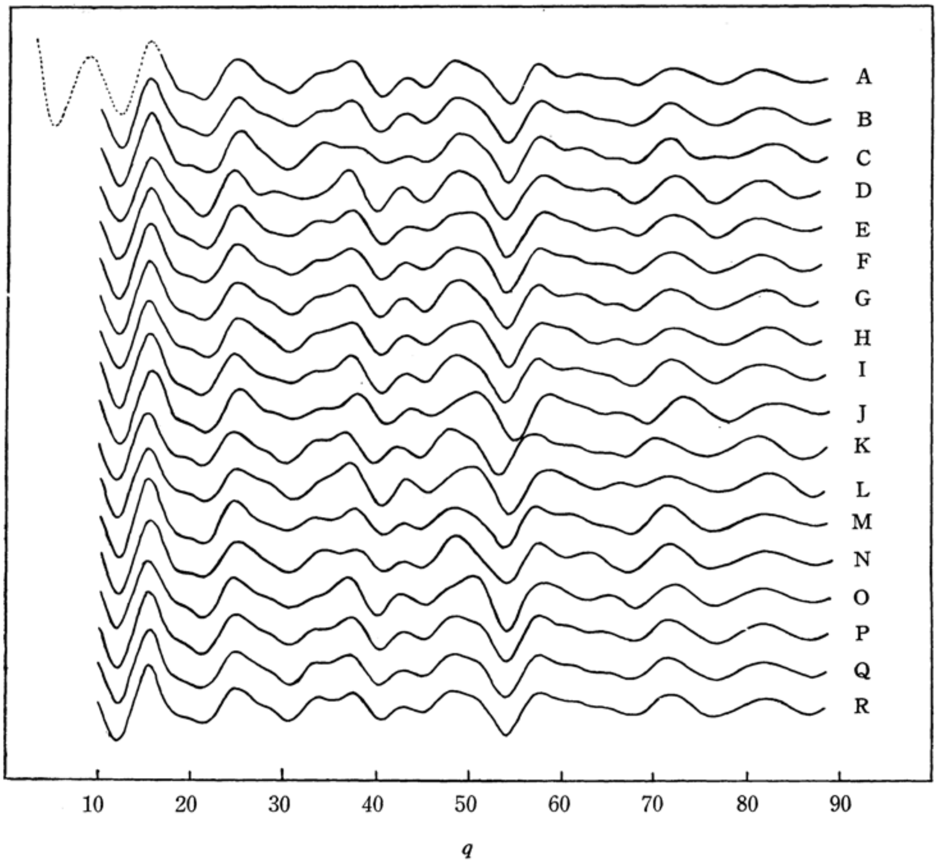

Fig. 4. Theoretical intensity curves of $CFCl_2—CFCl_2$

angles of 60°00′, 57°36′ and 55°12′, respectively.

As the parameter C—Cl gave large shifts for the positions of maxima and minima, the value of 1.76±0.01 Å was determined for the C—Cl distance. The relation between the depths of minima at $q=40.3$ and $q=45.0$ is very sensitive to the parameter ∠ClCCl. The feature of this region leads to the value of 110°30′±1° for the ∠ClCCl. The feature of the region $30<q<40$ is sensitive to the parameter ∠CCCl, C—F and C—C, while the feature of the region $47<q<52$ is sensitive to the parameter ∠FCCl, C—F and C—C. As the effects of these parameters appear in the same region, the limits of errors become somewhat larger for these parameters, especially for C—C. The values of C—F, C—C, ∠CCCl and ∠FCCl were determined as 1.38±0.02 Å, 1.54±0.06 Å, 112°±2° and 107°30′±1°30′, respectively. And the azimuthal angle and the amount of the *gauche* form were determined as 59°±4° and 55±10 per cent., respectively.

TABLE III

RESULTS OF ANALYSIS OF RADIAL DISTRIBUTION CURVE AND FINAL RESULTS FROM ADDITIONAL STUDY OF THEORETICAL INTENSITY CURVES

From radial distribution curve		Final results
Bond distance in Å		
C—F	1.37	1.38±0.02
C—C	1.54	1.54±0.06
C—Cl	1.76	1.76±0.01
Valency angle		
∠CCCl	112°	112°±2°
∠ClCCl	110°30′	110°30′±1°
∠FCCl	107°	107°30′±1°30′
Azimuthal angle of *gauche* form	55—63°	59°±4°
Amount of *gauche* form	52% at 15°C	55±10% at 15°C

Discussion of Results

Using infrared and Raman spectra, Kagarise and Daasch[7] investigated the energy difference between the isomers of the molecule under investigation. On the basis of the invariance of the spectrum with respect to temperature, they proposed two possible explanations of the spectroscopic data, neither of which is completely satisfactory. One is based on the assumption of a single molecular species corresponding to a largey energ difference, while

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[7] R. E. Kagarise and L. W. Daasch, *J. Chem. Phys.*, **23**, 113 (1955).

the other is based on the presence of two forms having an almost equal energy ($\Delta E < 300$ cal./mol.). Although a definite conclusion could not be obtained from the spectroscopic data, the existence of two isomeric forms was concluded from the result of the electron diffraction. The energy difference of the two isomers was calculated approximately from the obtained diffraction data by use of the following formula:

$$N_g/N_t=2\exp(-\Delta E/RT). \qquad (5)$$

The application of this formula leads to a value of 0—500 cal./mol. for the energy difference of the two isomers, the *trans* form being somewhat more stable than the *gauche* form. The result of the use of the electron diffraction method favors the second explanation proposed by Kagarise and Daasch.

A number of investigations on the molecular structures of organic fluorides indicated that the C—F and C—Cl bond lengths decrease with the number of fluorine atoms bonded with a carbon atom. The data on the molecular structures of some related compounds are listed in Table IV. Although $CFCl_2—CFCl_2$ is a difluoride, there is only one fluorine atom bonded with a carbon atom, and therefore C—F bond distance has almost the same value as that of a monofluoride. This fact indicates that the effect of substitution by fluorine atoms on the adjacent carbon atom is very small. The C—Cl bond distance in this molecule is affected scarcely at all by the fluorine atom, but it seems to be slightly shorter than the C—Cl bond in CH_2Cl_2 or $CHCl_3$, although this fact can not definitely be confirmed because of the uncertainty in the value of this distance.

TABLE IV

MOLECULAR STRUCTURES OF SOME RELATED COMPOUNDS

Compound	C—F (Å)	C—Cl(Å)	Method
CH_3Fa)	1.385		M. W.*
CH_2ClFb)	1.378±0.006	1.759±0.003	〃
$CHCl_2F$c)	1.41 ±0.03	1.73 ±0.04	V. E. D.**
CCl_3Fc)	1.40 ±0.04	1.76 ±0.02	〃
$C(CH_3)_3F$d)	1.38 ±0.02		V. E. D. & M. W.
CH_3CH_2Fe)	1.375±0.02		M. W.
$CCl_2F—CCl_2F$f)	1.38 ±0.02	1.76 ±0.01	S. E. D.***
CH_2F_2g)	1.358		M. W.
$CHClF_2$c)	1.36 ±0.03	1.73 ±0.03	V. E. D.
CCl_2F_2c)	1.35 ±0.03	1.74 ±0.03	〃
CHF_3h)	1.332±0.008		M. W.
$CClF_3$i)	1.328±0.002	1.751±0.004	S. E. D.
CF_4j)	1.323±0.005		S. E. D.
C_2F_6k)	1.32 ±0.01		〃
CH_3Cli)		1.783 ±0.003	S. E. D.
$C(CH_3)_3Cl$l)		1.80 ±0.01	〃
CH_2Cl_2m)		1.7724±0.0005	M. W.
$CHCl_3$h)		1.767	〃

* Microwave ** Visual electron diffraction *** Sector electron diffraction.

a) O. R. Gillam, H. D. Edwards and W. Gordy, *Phys. Rev.*, **75**, 1014 (1949).

b) N. Muller, *J. Am. Chem. Soc.*, **75**, 860 (1953).

c) L. O. Brockway, *J. Phys. Chem.*, **40**, 747 (1936).

d) F. Andersen, J. R. Andersen, B. Bak, O. Bastiansen, E. Risberg and L. Smedvik, *J. Chem. Phys.*, **21**, 373 (1953).

e) J. Kraitchman and B. P. Dailey, ibid., **23**, 184 (1955).

f) The present work.

g) D. R. Lide, *J. Am. Chem. Soc.*, **74**, 3548 (1952).

h) S. N. Ghosh, R. Trambarulo and W. Gordy, *J. Chem. Phys.*, **20**, 605 (1952).

i) L. S. Bartell and L. O. Brockway, ibid., **23**, 1860 (1955).

j) L. O. Brockway, C. G. Thornton and L. S. Bartell, *Am. Chem. Soc.*, Meeting, Los Angeles, California, March 1953.

k) See ref. 6.

l) O. Bastiansen and L. Smedvik, *Acta. Chem. Scand.*, **7**, 652 (1953).

m) R. J. Myers and W. D. Gwinn, *J. Chem. Phys.*, **20**, 1420 (1952).

Summary

The molecular structure of 1,2-difluorotetrachloroethane was studied by the electron diffraction method. The existence of the two isomeric forms, *trans* and *gauche*, was ascertained and the amount of the *gauche* form was found to be 55±10 per cent. This corresponds to the energy difference of 0—500 cal./mol. the *trans* form being more stable. The interatomic distances and the valency angles were determind as follows:

C—F=1.38±0.02 Å, C—Cl=1.76±0.01 Å, C—C=1.54±0.06 Å, ∠CCCl=112°±2°, ∠ClCCl=110°30′±1°, ∠FCCl=107°30′±1°30′, and the azimuthal angle of the *gauche* form=59°±4°.

The C—F bond distance in this molecule is greater than those distances of compounds having more than one fluorine atom bonded with a carbon atom. On the other hand, the C—Cl bond distance seems to be slightly shorter than those of chloroalkanes having no substituted fluorine atom.

The diffraction patterns and the microphotometer records were taken by using an apparatus in Nagoya University. The writers wish to express sincere gratitude to Professor M. Kubo, Professor R. Uyeda and Dr. M. Kimura for giving permission to use the apparatus and for their valuable advice. Thanks are also due to Mr. S. Shibata, Mr. H. Morimoto and Mr. K. Kimura of Nagoya University for their friendly assistance and to Mr. K. Kuchitsu and Mr. E. Hirota of Tokyo University for their help concerning a part of the calculations of the theoretical intensity by means of a punched card machine in the Division of Health and Welfare Statistics, Welfare Minister's Secretariat.

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