Electron Diffraction Investigation on the Molecular Structure of 1, 1, 2, 2-Tetrafluoro-1, 2-dichloroethane

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The molecular structure of some fluorochloroethanes presents two interesting problems. One of them is concerned with rotational isomerism, while the other with the effect of the neighboring halogene atoms on the C–F and C–Cl bond distances. In a previous publication¹⁾, the molecular structure of 1, 2-difluoro-1, 1, 2, 2-tetrachloroethane has been reported. This report presents the results of the determination of the molecular structure of 1,1,2,2-tetrafluoro-1,2-dichloroethane which was undertaken by the sector-microphotometer method of electron diffraction in order to find the effect of substitution with fluorine on the energy difference between isomers and on the bond distances.

The preliminary work²⁾ on this molecule was carried out merely by the radial distribution method on the assumption of a rather short distance of the C–C bond, 1.46 Å, which had been reported in early investigations on some fluorocarbons³⁾. Now, new experimental data obtained by use of an r^3-sector have been analysed by the correlation method as well as the radial distribution method without making any assumption about the C–C bond distance.

Experimental

The sample was prepared by Nagase in this laboratory from hexachloroethane, which was

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1) M. Iwasaki, S. Nagase and R. Kojima, This Bulletin, **30**, 230 (1957).

2) M. Iwasaki, S. Nagase and R. Kojima, *J. Chem. Phys.*, **22**, 959 (1954).

3) See Table VII.

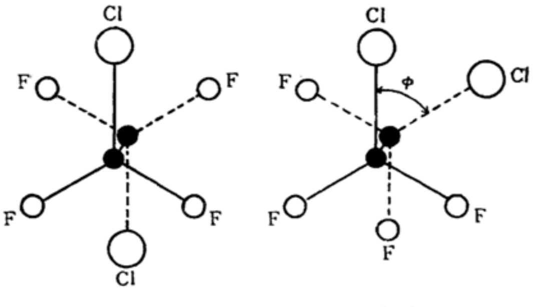
fluorinated with antimony trifluoride under a superatmospheric pressure in the presence of antimony pentachloride as a catalyst[4]. The product distilled at 3.8°C. The purity of this sample was tested with an infrared absorption spectrum. It was confirmed that the amount of $CFCl_2$-CF_3, that could not be removed by fractionation, was less than about 1∼2 per cent. Hence, its amount was so small as to affect the electron diffraction patterns in an inappreciable manner.

The diffraction patterns were obtained at a room temperature of about 10°C with an apparatus[5] having an r^3-sector, which was rapidly rotated during exposures. The apparatus used was essentially similar to that constructed by Ino[6]. The details will be reported elsewhere. Two nozzle-to-plate distances of 125 mm. and 285 mm. were used: the former was used for large-angle scattering while the latter for small-angle scattering. The extraneous scatterings were prevented by a beam trap fixed at the center of the sector. The wavelength of the electron beam was determined from the Debye rings of a gold foil to be about 0.055 Å. The sample was introduced into the electron beam through a fine nozzle which was surrounded by a trap cooled with liquid air to prevent the sample from spreading throughout the camera chamber. Diffration photographs were taken on Fuji Process Hard Plates with the consecutive exposures of 30∼60 sec. The photographic densities were measured up to a q value of about 100 by a Riken B-type recording microphotometer. In this measuremens, the photographic plate was rapidly rotated about the center of the diffraction pattern in order to average out the inevitable irregularities in the emulsion. The microphotometer traces thus obtained were measured by a coordinate comparator as a function of q. After calibrating the non-linearity of voltage-deflection relation of the electrometer in the microphotometer, the photographic density was converted into the relative intensity by the method similar to that employed by J. Karle and his coworker[7].

The molecular scattering intensity, I_m, was calculated from the total scattering, I_t, and a smooth background, I_b, that was drawn with the aid of the positivity criteria[7] as

$$I_m = I_t / I_b - 1 \qquad (1)$$

The averaged molecular scattering intensity qI_m shown by the top curve in Fig. 4 and Fig. 5 was obtained from several photographs with an average deviation of 4 per cent. of maximum amplitude, and it had an index of resolution of 0.95 to 1.00; that is, the ratio of the amplitude of the molecular scattering terms to the magnitude of the smooth background upon which the molecular terms are superposed is 0.95 to 1.00 times that given by theory for a perfect pattern.



trans form *gauche* form

Fig. 1. Stable configurations of CF_2Cl-CF_2Cl.

Analysis

Radial Distribution Curve.—The radial distribution (RD) curve shown in Fig. 2 was calculated by the following equation:

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

where I_m is the molecular scattering intensity. The artificial damping factor a was chosen so as $\exp(-aq^2)=0.1$ at $q=100$, and $q=(40/\lambda)\sin(\theta/2)$, where θ is the angle of scattering and λ is the wavelength of the electron beam.

In the calculation of the RD curves, a theoretical intensity curve with constant coefficients which was computed for the assumed model was substituted in place of the observed intensity below $q=18$. Several steps of successive approximations were taken in order to make the assumed model selfconsistent with the final RD curve which would satisfy Karle's criteria[7] as closely as possible.

The RD curve has maxima at 1.33_0, 1.74_5, 2.1—3.1, 3.48, 3.90 and 4.29 Å. The first two peaks at 1.33_0 and 1.74_5Å are assigned to C—F and C—Cl bond distances, respectively. The unresolved peak at 2.1—3.1 Å is due to the superposition of various non-bonded distances, while that at 3.48 Å to the *trans* F···F distance.

There are two conceivable configurations, i. e., the *trans* (C_{2h}) and the *gauche* (C_2) form, for this molecule as shown in Fig. 1. The peak at 3.90 Å corresponds to the *trans* F···Cl distance, which is characteristic of the *gauche* form, while the peak at 4.29 Å corresponds to the *trans* Cl···Cl distance which is characteristic of the *trans* form (see Fig. 1). Therefore, these two peaks evidently show the existence of two isomeric forms for this

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[4] R. Kojima, M. Iwasaki, S. Nagase and H. Baba, *Repts. Govt. Ind. Research Inst., Nagoya* (*Nagoya Kogyo Gijutsu Shikenjo Hokoku*).5, 225 (1956).

[5] Y. Morino, M. Kimura and M. Iwasaki, Lectured at the Sixth Annual Meeting of the Chemical Society of Japan, April 1953.

[6] T. Ino, *J. Phys. Soc. Japan*, **8**, 92 (1953).

[7] J. Karle and I. L. Karle, *J. Chem. Phys.*, **18**, 957 (1950).

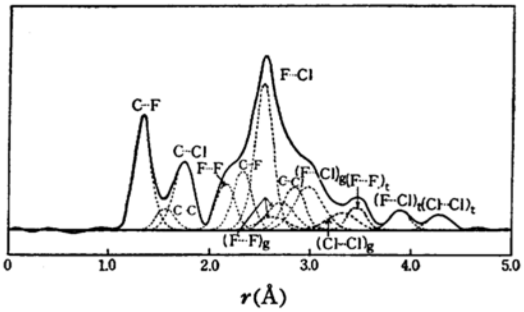

Fig. 2. Radial distribution curve for CF_2Cl-CF_2Cl (the full line). The dotted curves indicate individual peaks for the respective interatomic distances.

molecule. As the area under the RD peak is approximately proportional to Z_iZ_j/r_{ij}, the ratio of the two forms, N_t/N_g, can be calculated from the areas of the two peaks mentioned above by means of the following formula:

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

where Z_F and Z_{Cl} are the atomic numbers of fluorine and chlorine, $A_{Cl\cdots Cl}$ and $A_{F\cdots Cl}$ are the areas of the peaks, and $r_{Cl\cdots Cl}$ and $r_{F\cdots Cl}$ are *trans* Cl···Cl and *trans* F···Cl distances, respectively.

TABLE I

THE ASSUMED AND THE CALCULATED AMOUNT OF THE *GAUCHE* FORM IN ANALYSING THE RD CURVE

Assumed amount of the *gauche* form (%)	Calcd. amount of the *gauche* form (%)
60	54
50	49
45	46
35	42

In applying this formula, it was necessary to use the following procedure. Because the theoretical intensity with constant coefficients was used in place of the observed intensity below $q=18$ in the calculation of the RD curve, the ratio of the areas was affected by the assumed value of the abundance ratio of the two isomers. In order to see this effect, the RD curves were calculated on the assumption that the amount of the *gauche* form is equal to 60, 50, 45 and 35 per cent. The amount of the *gauche* form obtained from the areas of the RD peaks is shown in Table I for various cases. Table I shows that the self-consistent value was obtained from the RD curve if the amount of the *gauche* form was assumed to be equal to 50∼45 per cent. Therefore, the amount of the *gauche* form was estimated as 50∼45 per cent. from the RD curve. This value was further tested by the consideration of the theoretical intensity curves described in the next section.

In the range from 1.0 to 2.0 Å of the RD curve, a small peak corresponding to the C—C distance is masked by the skirts of prominent peaks on either side of the C—C peak. It seems to be unlikely that the contribution from the C—C distance affects the left side of the C—F peak as well as the right side of the C—Cl peak. Hence the right side of the former peak and the left side of the latter were fitted with Gaussian functions. The Gaussian curves which were fitted almost exactly to each side of the composite peak were subtracted from the composite peak. The remaining area formed a smooth curve having a maximum at 1.54 Å which was attributable to the C—C distance. The three components of the first peak of the RD curve are illustrated in Fig. 2. The areas of these decomposed peaks can favorably be compared with the theoretical values and fairly good agreement was obtained as shown in Table II.

TABLE II

THE RESULT OF ANALYSIS OF THE RD CURVE (THE REGION OF THE BONDED DISTANCES)

		C-F(Å)	C-C(Å)	C-Cl(Å)
Distance		1.33_0	1.54	1.74_5
Mean amplitude	obs.	0.052	0.045	0.061
	calc.	0.045	0.050	0.054
Peak area	obs.	1.00	0.18	0.70
	calc.	1.00	0.14	0.72

The portion of the RD curve from 2.1 to 3.7 Å corresponds to the superposition of the contributions from twelve interatomic distances in the *trans* as well as in the *gauche* form. This part of the RD curve was so complicated that the values of mean amplitudes and the peak heights could not be taken as unknown parameters in decomposing this part; hence the assumed values listed in Table II were used for the mean amplitudes, while for the peak heights the theoretical values calculated from the atomic numbers and the mean amplitudes were used. The amount of the *gauche* form was assumed to be 50 per cent. in accordance with the result obtained from the areas under peaks at 3.90 Å and 4.29 Å. As the left side of this peak (2.0∼2.4 Å) was composed of the contribution from the non-bonded F···F, C···F and F···Cl distances, these three distances were determined from the analysis of this part of the RD curve by trial and error on the assumption described above. The region from 2.4 Å to 3.0 Å was decomposed in a similar manner into contributions from non-bonded C···Cl, *gauche* F···F and *gauche* F···Cl distances. The remaining portion of the RD curve from 3.0 Å to 3.7 Å which was obtained by subtracting the contributions from the distances below 3 Å was, further, decomposed into contributions from the *gauche* Cl···Cl and *trans* F···F distances. These components lying between 2.0 and 3.7 Å are illustrated in Fig. 2. The molecular model which was constructed so as to satisfy the positions of the decomposed peaks as closely as possible, gave the set of interatomic distances listed in Table III. These interatomic distances are in good agreement with the respective RD peaks within 0.01∼0.02 Å. Moreover, the azimuthal angle of two C—Cl bonds of the *gauche* form can be estimated to be 62° from the *gauche* Cl···Cl distance. Although the amount of the *gauche* form was fixed at 50 per cent. in the foregoing analysis, the RD curve was affected, as mentioned above, by the assumed value of the abundance ratio of the isomers in the region for r larger than 2.7 Å. In order to see this effect, a number of theoretical and experimental RD curves were computed for various values of the abundance ratio as shown in Fig. 3. The theoretical RD curve shifts gradually from the full line to the dotted one with varying amounts of the *gauche* form from 30 to 70 per cent. On the other hand, the experimental RD curve falls in the shaded portion even if the assumed amounts of the *gauche* form were varied from 30 to 70 per cent. in calculating the theoretical part of the intensity. The discrepancy between the observed and the theoretical RD curve was minimized, when the amount of the *gauche* form was assumed to be about 50 per cent. This fact coincides with the results obtained from the areas of 3.90 and 4.29 Å peaks.

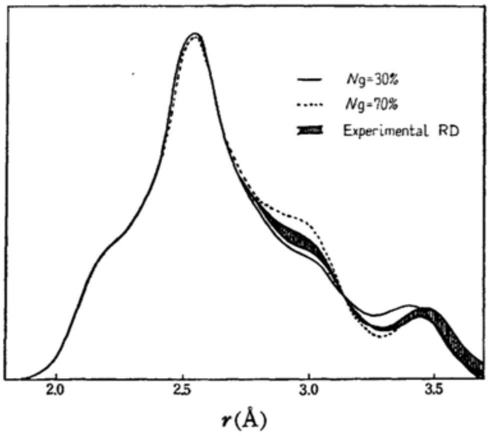

Fig. 3. Theoretical and experimental RD curves. The full line indicates the theoretical RD curve for the amount of the *gauche* form of 30%, and the dotted line for that of 70%. The shaded portion indicates the experimental RD curve, assuming the amount of the *gauche* form ranging from 30 to 70%.

The mean amplitudes listed in Tables II and III were obtained by fitting the RD peaks with Gaussian functions, no corrections being made for second order effects, such as a sample spread, multiple scatterings and the failure of Born approximation[8]. The observed mean amplitudes are in good agreement with those calculated by Morino et al.[9] from spectroscopic data.

Theoretical Intensity Curves. — The theoretical expression of the molecular scattering intensity obtained experimentally from Eq. 1 is given by the following equation:

$$qI_m(q)=\sum_{i\neq j}\sum(c_{ij}/r_{ij})\exp(-b_{ij}q^2)\times \sin(\pi q r_{ij}/10) \quad (4)$$

where r_{ij} denotes the interatomic distance between the i-th and the j-th atom and b_{ij} is the respective temperature factor which is calculated from its mean amplitude listed in Tables II and III. In the region of moderate and large q values, c_{ij} was considered to be constant proportional to Z_iZ_j, while in the region of small q,

$$c_{ij}=(Z_i-f_i)(Z_j-f_j)/\sum(Z_i-f_i)^2+S_i \quad (5)$$

was used, where Z_i is the atomic number, and f_i and S_i are the elastic and inelastic atomic scattering factors, respectively. The summations of Eq. 4 were performed by use of punchedcards and a Remington Rand Type-285 Model-2 tabulating machine[10,11]. Though the majority of the

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[8] R. Glauber and V. Schomaker, *Phys. Rev.*, **89**, 667 (1953); L. S. Bartell and L. O. Brockway, *Nature*, **171**, 978 (1953); J. A. Ibers and J. A. Hoerni, *Acta Cryst.*, **7**, 405 (1954).

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

[10] Y. Morino and K. Kuchitsu, *X-ray* (*X sen*), **8**, 37 (1954).

[11] The calculation by use of punched cards was carried out by Mr. K. Kuchitsu and Mr. E. Hirota of the University of Tokyo.

calculated values of the mean amplitudes listed in Tables II and III were those calculated by Morino et al.[9] from spectroscopic data, values for the non-bonded F⋯Cl and the *trans* F⋯Cl distances were appropriately taken 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_2F_6[12] and C_2Cl_6[13] by ascribing the contribution of torsional oscillation to the over-all vibration. For the *gauche* F⋯Cl distance, an appropriate value was also assumed using Karle's data.

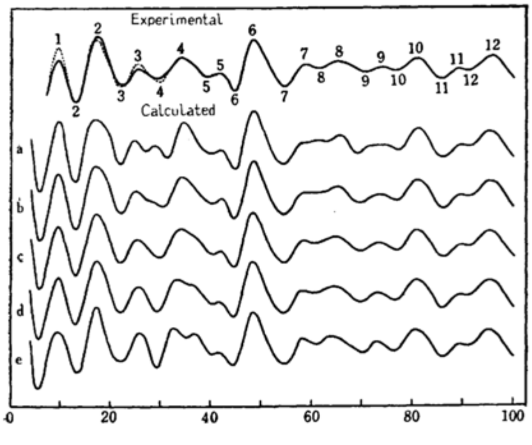

Fig. 4. Experimental and theoretical intensity curves for CF_2Cl-CF_2Cl. In the experimental curve, the dotted line indicates the correction for non-nuclear scatterings. Curves a and e indicate the theoretical intensity curves for the *trans* and the *gauche* form, respectively. Curves b, c and d indicate those for the amount of the *gauche* form of 30, 50 and 70%.

Theoretical intensity curves were computed for the *trans* and the *gauche* form using the values obtained from the RD curve ($C-F=1.33_0$, $C-Cl=1.74_5$, $C-C=1.54$, $\angle CCCl=112°$, $\angle FCCl=110°$, $\angle CCF=108°$ and the azimuthal angle of the *gauche* form$=63°$) on the assumption that the structural frame of the molecule does not change with rotation about the C—C bond. The curves a and e in Fig. 4 refer to the *trans* and the *gauche* form, respectively. These curves completely disagree with the experimental curve with respect to the features in the region $20<q<40$. The curves b, c and d represent isomeric mixtures, in which the amount of the *gauche* from is 30, 50 and 70 per cent., respectively. The fact that the curve c is in satisfactory agreement with experiments definitely confirms the amount of the *gauche* form estimated above from the RD curve.

In order to determine the range of inaccuracy in various structure parameters, a number of intensity curves were computed for various assumed models which have a C—F distance ranging from 1.31 to 1.38 Å, a C—C distance from 1.46 to 1.58 Å, a C—Cl distance from 1.70 to 1.79 Å, ∠CCF from 106°30′ to 111°, ∠CCCl from 109°30′ to 115°, and ∠ClCF from 104°30′ to 114°30′. Moreover, the azimuthal angle and the amount of the *gauche* form were varied for each assumed model.

In order to determine the limit of one structural parameter, it is desirable to

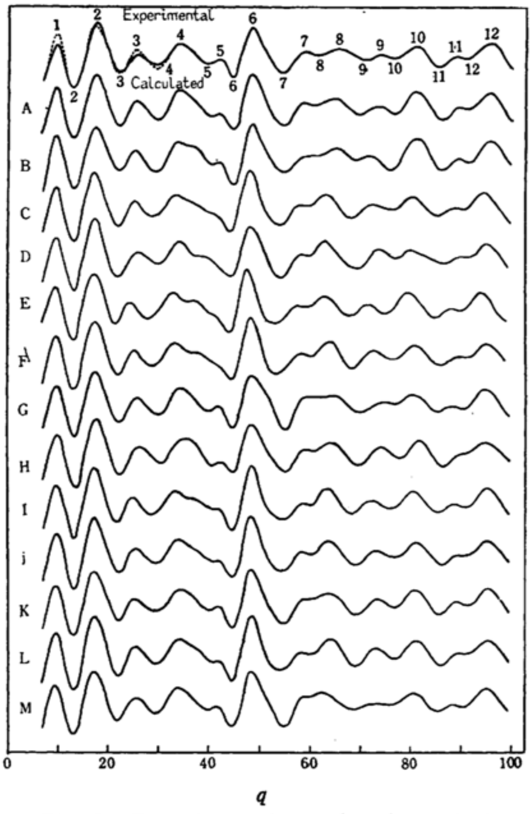

Fig. 5. Experimental and theoretical intensity curves for CF_2Cl-CF_2Cl. In the experimental curve, the dotted line indicates the correction for non-nuclear scattering. The molecular parameters used in the calculation are listed in Table IV.

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[12] D. A. Swick, I. L. Karle and J. Karle, *J. Chem. Phys.*, **22**, 1242 (1954).

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

TABLE III

THE RESULT OF ANALYSIS OF THE RD CURVE (THE REGION OF NON-BONDED DISTANCE)

						trans form			
		F···F	C···F	F···Cl	C···Cl	$(\mathrm{F}\cdots\mathrm{F})_g$	$(\mathrm{F}\cdots\mathrm{Cl})_g$	$(\mathrm{F}\cdots\mathrm{F})_t$	$(\mathrm{Cl}\cdots\mathrm{Cl})_t$
Distance	obs.	2.15	3.33	2.53	2.72	2.72	2.97	3.48	4.29
	calc.	2.16	2.33	2.53	2.73	2.70	2.98	3.46	4.31
Mean amplitude	obs.	—	—	—	—	—	—	—	0.088
	calc.	0.056	0.059	0.065	0.073	0.114	0.120	0.061	0.074

		gauche form					
		$(\mathrm{F}\cdots\mathrm{F})_g$	$(\mathrm{F}\cdots\mathrm{F})_g$	$(\mathrm{F}\cdots\mathrm{Cl})_g$	$(\mathrm{Cl}\cdots\mathrm{Cl})_g$	$(\mathrm{F}\cdots\mathrm{F})_t$	$(\mathrm{F}\cdots\mathrm{Cl})_t$
Distance	obs.	2.62	2.72	2.97	3.30	3.48	3.90
	calc.	2.63	2.71	2.98	3.31	3.46	3.88
Mean amplitude	obs.	—	—	—	—	—	0.062
	calc.	0.114	0.114	0.120	0.125	0.061	0.074

TABLE IV

MOLECULAR PARAMETERS USED IN CALCULATING THE THEORETICAL INTENSITY CURVES SHOWN IN FIG. 5

Model	C—F	C—C	C—Cl	∠CCCl	∠CCF	∠FCCl
A (RD)	1.33_0Å	1.54Å	1.74_5Å	112°	108°	110°
B	1.31	1.54	1.75	112	108	110.5
C	1.35	1.54	1.75	112	108	110.5
D	1.35	1.54	1.73	112	108	110.5
E	1.35	1.54	1.77	112	108	110.5
F	1.34	1.48	1.74	112	108	110.5
G	1.34	1.58	1.74	112	108	110.5
H	1.34	1.54	1.74	112	108	109
I	1.34	1.54	1.74	112	108	111.5
J	1.34	1.54	1.74	111	108	110.5
K	1.34	1.54	1.74	113	108	110.5
L	1.34	1.54	1.74	112	107	110.5
M	1.34	1.54	1.74	112	109	110.5

select the regions in which the intensity curve is unaffected by other parameters. If such regions were not found and the effects of several parameters overlapped, the contribution from other parameters must be considered properly. Some of the computed curves are reproduced in Fig. 5 in order to illustrate the dependence of relative positions and intensities of maxima and minima upon the parameters. The values of the parameters used are listed in Table IV except the amount of the *gauche* form and the azimuthal angle which are kept constant at 50 per cent. and 63°, respectively.

C—F and C—Cl Parameters. — The position of the 6th maximum and the relative depth of 3rd and 4th minima depend mainly upon the C—F and C—Cl parameters[14]. This relation gives the acceptable region in the parameter chart illustrated in Fig. 6. The full lines refer to the position of the 6th maximum, and the broken lines the relative depth of 3rd and 4th minima. The area enclosed by these border lines is the acceptable domain. The positions of dots indicate the parameters of the models for which intensity curves were computed.

C—C Parameter. — The changes of the intensity curves caused by the variation of the C—C parameter, can be improved by the modification of other parameters, because there is no region in which the intensity curve depends solely upon the C—C parameter. In other words, it means that the contribution from the C—C distance is very small. However, the modification of the C—F or the C—Cl parameter makes the position of the 6th maximum shift out of the limit of the experimental error, because the position of the 6th maximum does not depend upon the C—C parameter. Although the change in the C—C distance is accompanied by the changes in the interatomic distances

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[14] The intensity relation between 3rd and 4th minima depends also upon the abundance ratio of the isomers but the changes are not serious in the region of the amount of the *gauche* form from 40 to 60 per cent.

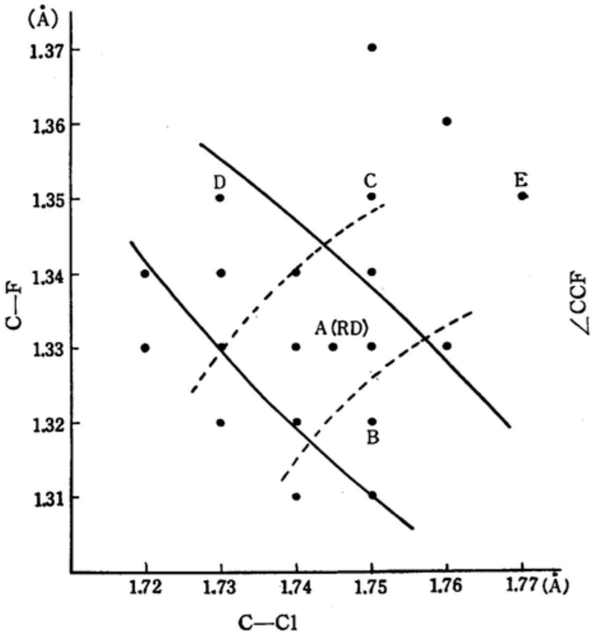

Fig. 6. Parameter chart. The positions of dots indicate the parameters of models for which intensity curves were computed. The positions of letters indicate the parameters of models for which intensity curves are shown in Fig. 5.

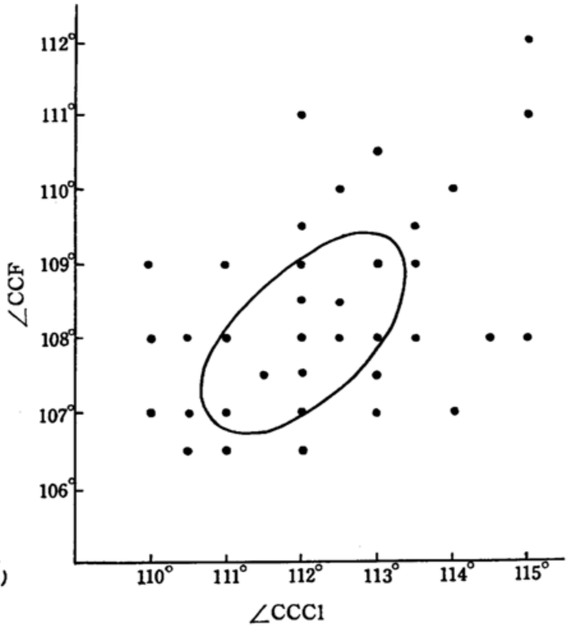

Fig. 7. Parameter chart. The positions of dots indicate the parameters of models for which intensity curves were computed. The area enclosed by the curved line roughly indicates the acceptable region.

TABLE V

COMPARISON BETWEEN EXPERIMENTAL AND THEORETICAL INTENSITY CURVES

Peak		Peak position			Peak height		
min.	max.	q_0	q_c	q_c/q_0	I_0	I_c	I_0/I_c
3		22.0	22.0	1.000	−1.00	−1.12	0.893
	3	25.4	25.4	1.000	+0.42	+0.36	1.167
4		29.5	29.6	1.003	−0.70	−0.82	0.854
	4	33.9	33.9	1.000	+0.86	+1.04	0.827
5		39.5	40.2	1.018	−0.44	−0.56	0.786
	5	41.6	41.8	1.005	−0.29	−0.41	0.707
6		44.5	44.5	1.000	−1.31	−1.42	0.923
	6	48.3	48.3	1.000	+1.87	+2.06	0.908
7		54.7	54.5	0.996	−0.06	−1.11	0.955
	7	58.3	58.3	1.000	+0.46	+0.25	(1.840)
8		61.3	60.6	0.989	+0.05	+0.11	(0.455)
	8	65.0	65.0	1.000	+0.54	+0.50	1.080
9		70.4	69.7	0.990	−0.22	−0.49	(0.449)
	9	74.0	73.5	0.993	+0.11	+0.07	(1.571)
10		76.9	76.7	0.997	−0.13	−0.42	(0.310)
	10	80.8	81.0	1.002	+0.62	+0.94	0.660
11		85.6	86.0	1.005	−0.66	−0.84	0.786
	11	89.1	89.4	1.003	+0.02	−0.05	(——)
12		91.0	91.0	1.000	−0.14	−0.14	(1.000)
	12	95.6	95.4	0.998	+0.78	+0.84	0.929
Average				1.000			0.883
Average deviation				0.003			0.104

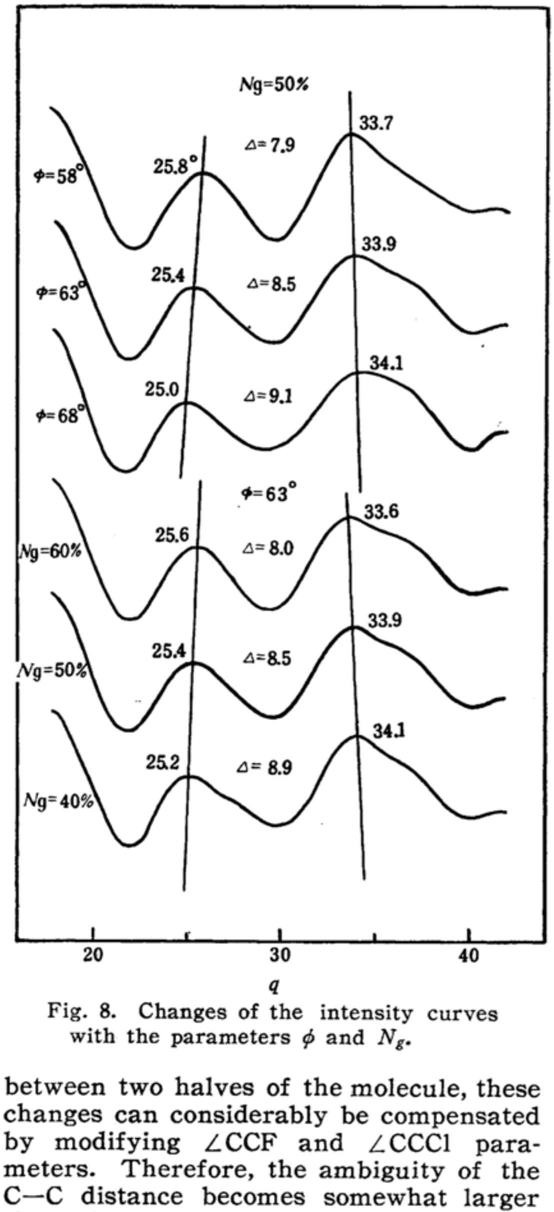

Fig. 8. Changes of the intensity curves with the parameters ϕ and N_g.

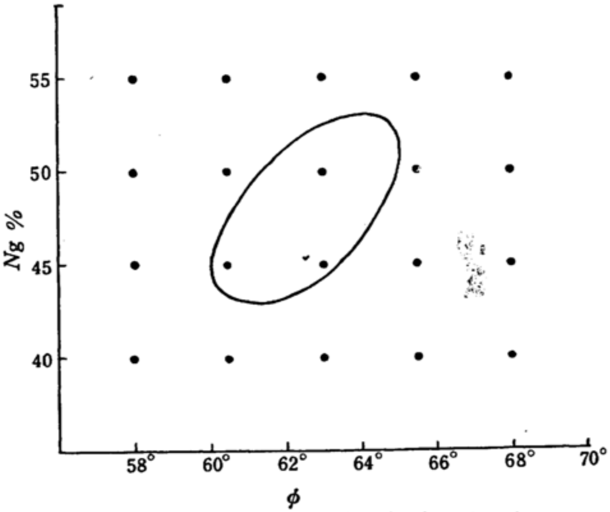

Fig. 9. Parameter chart for the fractional abundance and the azimuthal angle of the *gauche* form. The positions of dots indicate the parameters of models for which intensity curves were computed.

between two halves of the molecule, these changes can considerably be compensated by modifying ∠CCF and ∠CCCl parameters. Therefore, the ambiguity of the C—C distance becomes somewhat larger than those of other parameters. The acceptable models could be obtained for the C—C distance ranging from 1.50 to 1.58 Å by means of the suitable combination of other parameters.

∠FCCl Parameter. — This parameter affects sensitively the position of the 9th maximum and the depth of the 6th minimum. The models with ∠FCCl larger than 111° were unacceptable in the position of the 9th maximum, even if various combinations of other parameters, C—Cl or C—C, were considered. The lower limit of ∠FCCl was obtained from the depth of the 6th minimum which depends only upon this parameter. The 6th minimum is too shallow compared with the experiment for the model with ∠FCCl smaller than 109°. This fault could not be improved by adjusting other parameters.

∠CCF and ∠CCCl Parameters. — As stated above, the effects of ∠CCF and ∠CCCl parameters are compensated by the C—C parameter. Projecting the three dimensional parameter chart composed of the ∠CCF, ∠CCCl and C—C parameters to a ∠CCF—∠CCCl plane, the domain shown in Fig. 7 was obtained as a result of the superposition of a number of domains which are acceptable for various values of the C—C parameter.

The Abundance Ratio and the Azimuthal Angle. — The positions of the 3rd and the 4th maximum depend upon many other parameters, but the interval between these two maxima depends only upon the abundance ratio and the azimuthal angle as shown in Fig. 8. Therefore, this interval can be used to determine the limits of these parameters. Because the positions of the 3rd the 4th maximum can precisely be measured by use of the long camera length, those parameters were determined with considerably little ambiguity, as shown in Fig. 9.

From the analysis described above, the best model and the limits of ambiguity were estimated as follows:

$\mathrm{C{-}F} = 1.33_0 \pm 0.01_5$ Å ∠CCF = 108° ± 1°30′
$\mathrm{C{-}C} = 1.54 \pm 0.04$ Å ∠CCCl = 112° ± 1°30′
$\mathrm{C{-}Cl} = 1.74_5 \pm 0.01_5$ Å ∠FCCl = 110° ± 1°

The azimuthal angle of the *gauche* form $=62.5\pm3°$

The amount of the *gauche* form $=48\pm5$ per cent. at 10°C.

For the best model the mean value of $q_{\text{calc.}}/q_{\text{obs.}}$ and $I_{\text{obs.}}/I_{\text{calc.}}$ for the maxima and the minima are 1.000 and 0.883 with the average deviation of 0.003 and 0.104, respectively. (See Table V.)

Discussion of the Results

It is interesting to compare the C—F and C—Cl bond distances obtained in this investigation with those on other chlorofluorocompounds having different numbers of fluorine atoms. As shown in Table VI, the C—F distance in a $CF_2Cl—CF_2Cl$ molecule lies between the value of 1.32 Å in $CF_3—CF_3$[12] and that of 1.38 Å in $CFCl_2—CFCl_2$[1]. On the other hand, although the inaccuracy of the data does not permit to draw a definite conclusion, it appears that the C—Cl distance of $CF_2Cl—CF_2Cl$ is shorter than that of C_2Cl_6[15] and $CFCl_2—CFCl_2$[1]. This fact coincides with the results from a number of investigations on the molecular structures of organic fluorine compounds[16] in which the C—F and C—Cl bond distances decrease with the number of the fluorine atoms bonded with the same carbon atom.

TABLE VI

C-F AND C-Cl BOND DISTANCES IN SOME FLUOROCHLOROETHANES

Molecule	C-F (Å)	C-Cl (Å)
CF_3-CF_3	1.32 ± 0.01[12]	
CF_2Cl-CF_2Cl	$1.33_0 \pm 0.01_5$*	$1.74_5 \pm 0.01_5$*
$CFCl_2$-$CFCl_2$	1.38 ± 0.02[1]	1.76 ± 0.01[1]
CCl_3-CCl_3		1.77 ± 0.02[15a]
		$1.76_3 \pm 0.01$[15b]

* Present work.

An abnormal shortening of the C—C bond distance has been reported[17,18] in the early investigations of some organic fluorine compounds as shown in Table VII. However, the recent investigations by Karle[12] and Livingston[19-21] have shown that several fluorine compounds listed in the table have almost normal distances of the C—C bond. Although in the preliminary analysis the abnormally short distance of the C—C bond was assumed, it was found from this more precise analysis that the experimental results could be explained by a normal value of the C—C distance in this molecule. However, because of great inaccuracy of the determination of this distance, a definite conclusion could not be given for the problem of the effect of halogen atoms on the C—C bond distances in organic halides.

TABLE VII

C-C BOND DISTANCES IN SOME FLUOROCARBONS

Molecule	Early results	Recent results
CF_3-CF_3	1.45 ± 0.06[17]	1.56 ± 0.03[12]
		1.51 ± 0.06[19]
CH_3-CF_3	1.45 ± 0.04[17]	1.53 ± 0.04[17]
		1.52 ± 0.04[20]
CF_3-C_2H_5	1.49 ± 0.04[18]	
CF_3-CF_2-CF_3	1.47 ± 0.03[18]	
CHF_2-CHF_2	1.46 ± 0.05[18]	
CH_3-CF_2-CH_3	1.51 ± 0.02[18]	
	1.48 ± 0.03[18]	
CF_3-CH_2Cl	1.47 ± 0.03[18]	
CF_3-CCl_3	<1.54[18]	
CF_3CH_2OH		1.52 ± 0.04[21]
CF_2Cl-CF_2Cl		1.54 ± 0.04*

* Present work.

It is to be noted that the value of ∠FCF somewhat smaller than the tetrahedral angle as reported in many organic fluorine compounds except carbon tetrafluoride, seems to be revealed also in this molecule, that is, the value of 108°44′ obtained from other angle parameters is consistent with those in CH_2F_2(108°17′)[22], in CCl_2F_2(109°)[23], and in many other compounds containing a CF_3 group[24].

The problem of the rotational isomerism

15a) Y. Morino and M. Iwasaki, *J. Chem. Phys.*, **17**, 216 (1949).

15b) Y. Morino and E. Hirota, ibid., **28**, 185 (1958).

[16] The C—F and the C—Cl distances in many organic fluorine compounds were tabulated in a previous paper. (See ref. 1.)

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[21] R. L. Livingston and G. Vanghan, ibid., **78**, 2711 (1956).

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[23] L. O. Brockway, *J. Phys. Chem.*, **40**, 747 (1936). According to a recent study by R. L. Livingston and D. H. Lyon (*J. Chem. Phys.*, **24**, 1283 (1956)), the value of 109.5°±3° was obtained. At any rate, because these two values from the visual method of electron diffraction are not free from great uncertainty, more accurate studies by the microwave spectroscopy or the sector—microphotometer method of electron diffraction are desired for the elucidation of the structure of this molecule.

[24] Many examples of the data for ∠FCF in the compounds containing a CF_3 group are cited in ref. 20.

in this molecule has previously been studied by several investigators. On the basis of a number of observed Raman lines, Glockler and Sage[25] conculuded that two isomeric forms were present in the liquid state. Simpson and Plyler[26] have studied the infrared spectrum in the vapor state, and carried out a partial assignment on the basis of two isomeric forms. Kagarise[27] has recently studied the dependence of infrared spectra on temperature and state, and concluded that the *trans* isomer persists in the crystalline solid, and is the stable form in the liquid and the vapor state. The energy difference between the isomers in the vapor state was reported to be 500± 200 cal./mol.

The energy difference, ΔE, was also obtained from the diffraction data by use of the following formula:

$$\frac{N_g}{N_t}=2\frac{f_g}{f_t}\exp(-\Delta E/\boldsymbol{R}T) \qquad (6)$$

where f_t and f_g are the vibrational and rotational partition functions of the *trans* and the *gauche* molecules. The factor 2 is introduced to account for the double weight of the *gauche* form. The ratio of f_g to f_t is considered to be approximately equal to unity. Therefore, neglecting the difference between f_g and f_t, the value of 440±110 cal./mol. is obtained from the diffraction data. This result is in good agreement with the value of 500±200 cal. /mol. obtained by Kagarise in the vapor state from the temperature dependence of the infrared spectra.

The energy difference for the molecule in question is smaller than the value of 1140 cal./mol.[28] for a CH_2Cl-CH_2Cl molecule in contrast to the fact that methyl substitution[29] does not seriously decrease the energy difference. This lowering of the energy difference is probably caused by the fact that the dipole interaction is not much different between the *trans* and the *gauche* position as a result of the substitution of C—H with C—F, the bond moment of which is almost equal to that of a C—Cl bond. This fact is consistent with the conclusion proposed by Mizushima, Morino and Shimanouchi[30] that the steric repulsion plays an important role in determining the potential barrier but the electrostatic force is the important factor in determining the energy difference between the various configurations. Miyagawa[31] and Kreevoy et al.[32] supported this conclusion by a quantitative calculation.

Summary

The molecular structure of 1,1,2,2-tetrafluoro-1,2-dichloroethane was investigated by means of the sector-microphotometer method of electron diffraction. The existence of two isomeric forms, i.e., *trans* and *gauche*, was confirmed, and the amount of the *gauche* form was found to be 48±5 per cent. at 10°C. This corresponds to the energy difference of 440±110 cal./mol., the *trans* form being more stable than the *gauche* form. The interatomic distances and the bond angles were determined as follows:

$\text{C—F} = 1.33_0 \pm 0.01_5 \text{Å} \quad \angle\text{CCF} = 108° \pm 1°30'$

$\text{C—C} = 1.54 \pm 0.04 \text{Å} \quad \angle\text{CCCl} = 112° \pm 1°30'$

$\text{C—Cl} = 1.74_5 \pm 0.01_5 \text{Å} \quad \angle\text{FCCl} = 110° \pm 1°$

and the azimuthal angle of the *gauche* form = 62.5°±3°.

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