Electron Diffraction Investigation on the Molecular Structure of 1,1,2-Trifluoro-1,2,2-trichloroethane

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(Received August 5, 1958)

In previous publications[1-3] it has been reported that the energy difference between *trans* and *gauche* isomer for 1,2-difluoro-1,1,2,2-tetrachloroethane is 0~500 cal./mol., and that for 1,1,2,2-tetrafluoro-1,2-dichloroethane is 440±110 cal./mol. In order to compare these results with the data for the well-known series of chlorinated ethanes[4] (CH_2Cl-CH_2Cl, $CHCl_2$-CH_2Cl and $CHCl_2CHCl_2$), it is desirable to elucidate the molecular structure of 1,1,2-trifluoro-1,2,2-trichloroethane. However, the problem of rotational isomerism in this molecule has not yet been studied except when an earlier study was made by Glockler and Sage[5]. Based solely on the number of observed Raman lines, they concluded that two isomers were present, but no attempt was made at the determination of the energy difference between the two isomers.

This report presents the results of studies on the molecular structure of CF_2Cl-$CFCl_2$ carried out by the sector-microphotometer method of electron diffraction mainly to find the effect of fluorine substitution on the energy difference between the two isomers. An attempt was also made at the determination of the equilibrium angle of the stable configuration.

Experimental

The sample was prepared by S. Nagase in this laboratory from hexachloroethane, which was fluorinated with antimony trifluoride under superatmospheric pressures in the presence of antimony pentachloride as a catalyst[6]. The product distilled at 47.8°C. The purity of this sample was tested with an infrared absorption spectrum and there were no absorptions due to impurities.

The diffraction patterns were taken at a room temperature of about 20°C using an apparatus[7] having an r^3-sector, which was rapidly rotated during photographic exposure. The apparatus and the experimental procedures were the same as described in the previous paper[3]. Two nozzle-to-plate distances of 125 mm. and 285 mm. were used: the former was used for large angle scattering and the latter for small angle scattering, which was sensitive to the internal rotation. The wavelength of the electron beam was about 0.055Å. The extraneous scatterings were removed by a beam trap and the spreading of the sample was prevented by a trap cooled with liquid air.

The molecular intensity curve qI_m shown by the top curve in Fig. 5 was obtained by the method similar to that employed by Karle and his coworker[8], the index of resolution being about 1.0.

Analysis

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

$$f(r)=\sum_{q=0}^{q_{\max}} qI_m \exp(-aq^2)\sin(\pi qr/10) \qquad (1)$$

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

In the calculation of the RD curve, a theoretical intensity curve which was computed with constant coefficients for the assumed model was substituted in place of the observed intensity below $q=6$. Furthermore, a correction for the effect of non-nuclear scatterings[9] was made. The RD curve shown in Fig. 2 was obtained after several steps of successive

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

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

[3] M. Iwasaki, This Bulletin, **31**, 1071 (1958).

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[5] G. Glockler and C. Sage, *J. Chem. Phys.*, **9**, 387 (1941).

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

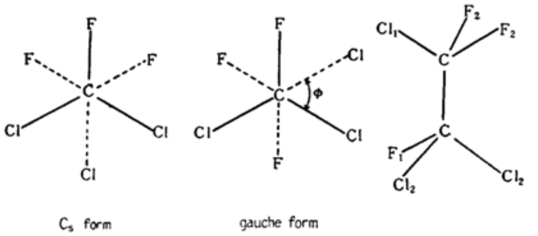
[7] Y. Morino, M. Kimura and M. Iwasaki, The Sixth Annual Meeting of the Chemical Society of Japan, April 1953.

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

[9] L. S. Bartell, L. O. Brockway and R. H. Schwedeman, ibid., **23**, 1854 (1955).

approximations based on Karle's criteria[8].

The RD curve has maxima at 1.34_5, 1.75_5, 2.0~3.7, 3.89_0, and 4.31_3Å. The first two peaks at 1.34_5 and 1.75_5Å are assigned to C—F and C—Cl bond distances, respectively. The unresolved peak at 2.0~3.7Å is due to the superposition of various non-bonded distances, that at 3.89_0Å to the *trans* F···Cl distance, and that at 4.31_3Å to the *trans* Cl···Cl distance.



C_s form   gauche form

Fig. 1. Rotational isomers of CF_2Cl-$CFCl_2$.

Two configurations are conceivable for this molecule. One of them is a form having the C_s symmetry as shown in Fig. 1. This form will be called the C_s form. The other form having no symmetry is called the *gauche* form. Because the *trans* Cl···Cl distance is characteristic of the *gauche* form, the peak at 4.31_3Å evidently shows the existence of the *gauche* form. On the other hand, the *trans* F···Cl distance appears in both forms, but the number of this distance is three for the C_s form whereas it is one for the *gauche* form. Therefore, the ratio of the areas under these two peaks is expected to depend on whether there exists only the *gauche* form or whether two isomers exist. Because the area under the RD peak is approximately proportional to Z_iZ_j/r_{ij}, the ratio of the two forms, N_{C_s}/N_g, can be calculated from the areas of the two peaks mentioned above by means of the following formula:

$$\frac{N_{C_s}}{N_g}=\frac{Z_{Cl}r_{F\cdots Cl}A_{F\cdots Cl}}{3Z_Fr_{Cl\cdots Cl}A_{Cl\cdots Cl}}-\frac{1}{3} \qquad (2)$$

where Z_F and Z_{Cl} are, respectively, 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 the *trans* Cl···Cl and the *trans* F···Cl distances. The ratio of the areas was hardly affected at all by the assumed value of the abundance ratio of the two isomers, because the correction for non-nuclear scatterings made it possible to use the observed values to such a small q value as 7. In this way, the amount of the *gauche* form was estimated as 80 per cent from the RD curve in applying Eq. 1. This value was further tested by the consideration of theoretical intensity curves described in the next section.

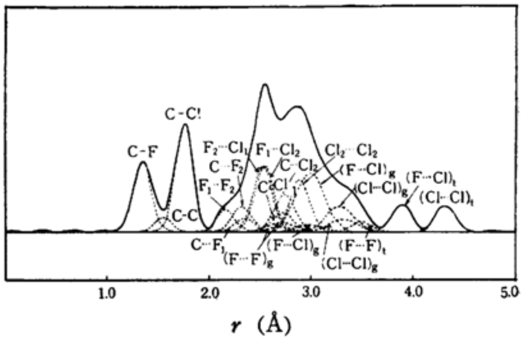


Fig. 2. Radial distribution curve for CF_2Cl-$CFCl_2$.

When the contributions from the C—F and C—Cl distances were subtracted from the composite peak ranging from 1.0 to 2.0Å, the remaining area forms a smooth curve having a maximum at 1.54_5Å which is attributable to the C—C bond distance. These three components of the first composite peak of the RD curve are illustrated in Fig. 2, and the areas under these peaks are in good agreement with the theoretical values shown in Table I.

According to the results of the previous reports[1-3] and many other papers about fluorochloromethane[10], the C—F and the C—Cl bond distances decrease with the number of fluorine atoms bonded with one and the same carbon atom. Therefore, the C—F and the C—Cl bond distances may probably be different for two halves of this molecule. In fact, the values of 1.38Å (C—F) and 1.76Å (C—Cl) in $CFCl_2$-$CFCl_2$, and those of 1.33_0Å (C—F) and 1.74_5Å (C—Cl) in CF_2Cl-CF_2Cl being assumed for the two halves of this molecule, the weighted mean values of the C—F and the C—Cl distances were 1.34_7 and 1.75_5Å, respectively; those values are in good agreement with the observed values of 1.34_5 and 1.75_5Å.

In analyzing the part of the RD curve from 2.0 to 3.7Å, an assumption was made that the bonded distances and the bond angles in two halves of the molecule were equal to those of $CFCl_2$-$CFCl_2$ and CF_2Cl-CF_2Cl, respectively. Furthermore, the

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[10] The C-F and the C-Cl distances in many organic fluorine compounds have been tabulated in the previous paper, ref. 2.

TABLE I
THE RESULT OF ANALYSIS OF THE RD CURVE
(THE DISTANCES ARE GIVEN IN Å UNITS)

		C—F	C—C	C—Cl	$(F\cdots Cl)_t$	$(Cl\cdots Cl)_t$
Distance		1.34_4	1.54_5	1.75_5	3.89_0	4.31_3
Mean amplitude.	obs.	0.055_5	0.041_7	0.054_0	0.063_8	0.069_5
	calc.	0.045	0.050	0.054	0.070	0.074
c_{ij}	obs.	0.259	0.055	0.514	0.307	0.335
	calc.	0.255	0.057	0.481	0.337	0.364

assumed values listed in Table II were used for the mean amplitudes. When contributions from distances that do not change with internal rotation were subtracted from the experimental RD curve, the remaining curve shown in Fig. 3 was obtained, the part from 2.4 to 3.7Å of this curve corresponding to the contribution from the *gauche* F···F, the *gauche* F···Cl, the *gauche* Cl···Cl, and the *trans* F···F distances, which change with the azimuthal angle of the *gauche* form and the relative amount of rotational isomers. The fact that the part of the remaining curve from 2.0 to 2.4Å which is attributable to the contribution from the distances that are independent of the internal rotation, is almost equal to zero reflects the correctness of the assumption about the bonded distances and bond angles. When the remaining curve thus obtained was compared with the theoretical one calculated for various azimuthal angles[11], ϕ, of the *gauche* form, the curve for $\phi=60°$ was found to be in good agreement with the observed one as shown in Fig. 3.

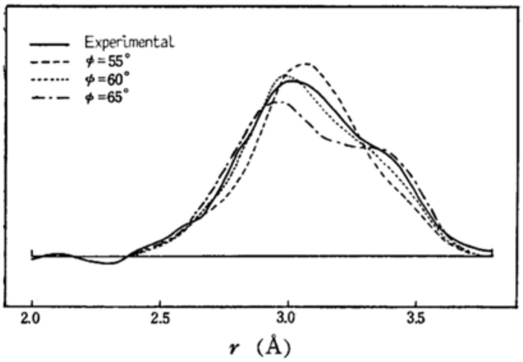

Fig. 3. Comparison between the experimental and the calculated RD curves which are attributable to the contributions from the distances that vary with the internal rotation.

TABLE II
MEAN AMPLITUDES USED IN THIS ANALYSIS
(IN Å)

Distance	Mean amplitude	Distance	Mean amplitude
C—F	0.045	(F···F)	0.114
C—C	0.050	$(F\cdots Cl)_g$	0.120
C—Cl	0.054	$(Cl\cdots Cl)_g$	0.125
F···F	0.056	$(F\cdots F)_t$	0.061
C···F	0.059	$(F\cdots Cl)_t$	0.070
F···Cl	0.065	$(Cl\cdots Cl)_t$	0.074
C···Cl	0.073		
Cl···Cl	0.070		

The mean amplitudes listed in Table I 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[12]. The observed mean amplitudes are in good agreement with those calculated by Morino et al.[13] from spectroscopic data.

Theoretical Intensity Curves. — The theoretical intensity curves were calculated using the following equation:

$$qI_m(q)=\sum_{i\neq j}\sum(c_{ij}/r_{ij})\times\exp(-b_{ij}q^2)\sin(\pi q r_{ij}/10) \tag{3}$$

where r_{ij} denotes the interatomic distance between i-th and j-th atoms, b_{ij} is the temperature factor, and

$$c_{ij}=Z_iZ_j/\sum_i(Z_i^2+Z_i) \tag{4}$$

In the region of small q-values the effect of non-nuclear scattering was corrected for the experimental intensity and then the constant coefficient was used over the whole q region in calculating theoretical intensity curves. The summations of Eq. 3 were performed by use of punched cards and a Remington Rand Type-285 Model-2 Tabulating machine[14,15].

In determining the range of uncertainty of 13 structural parameters and 14 mean

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[11] The azimuthal angle of the *gauche* form is that for the two C-Cl bonds in the molecule.

[12] 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).

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

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

[15] The calculation by use of punched cards was carried out by K. Kuchitsu of the University of Tokyo.

amplitudes, it was not feasible to exhaust the possible variations in all parameters. Therefore, all the parameters except the ratios, $\rho_{Cl}=C-Cl_2/C-Cl_1$ and $\rho_F=C-F_1/C-F_2$ the azimuthal angle of the *gauche* form, ϕ, and the fraction of the *gauche* form, N_g, were kept constant throughout the analysis. The mean amplitudes used were the same as those in the previous papers[2,3]. The majority of these values listed in Table II were taken from those calculated by Morino et al.[13] from spectroscopic data or obtained by Karle et al.[16,17] from electron diffraction experiments. The C—C distance and all the bond angles were assumed to be equal to those in $CFCl_2$-$CFCl_2$ and CF_2Cl-CF_2Cl, that is, C—C=1.54Å, $\angle CCCl_1=\angle CCCl_2=112°$, $\angle CCF_1=107°05'$, $\angle CCF_2=108°$, $\angle F_1CCl_2=107°30'$, $\angle F_2CCl_1=110°$, $\angle F_1CFl_2=108°44'$ and $\angle Cl_1CCl_2=110°30'$. It was already shown in the RD analysis that this assumption was quite adequate.

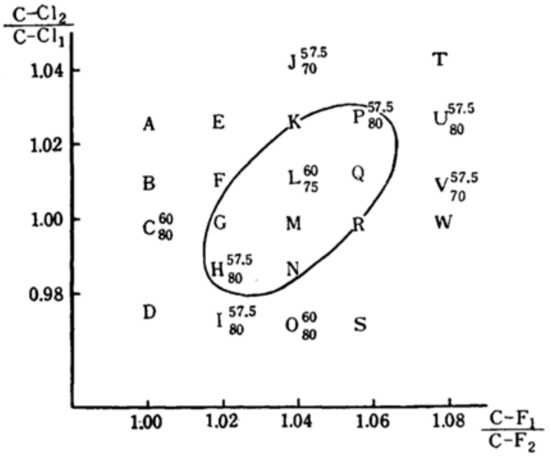

Fig. 4. Parameter chart. The positions of letters indicate the parameters of models for which intensity curves were computed. The values of the superscripts and the subscripts indicate the azimuthal angles and the amounts of the *gauche* form both of which were used in calculating the intensity curves reproduced in Fig. 5.

For each model indicated in a $\rho_{Cl}-\rho_F$ parameter chart (Fig. 4), parameters, ϕ and N_g, were further varied. The projection of the $\rho_{Cl}-\rho_F$ parameter chart on a $\phi-N_g$ plane is shown in Fig. 6. Some of the computed curves are reproduced in Fig. 5. The relative depth of the 5th and the 6th minimum, the position of the 3rd maximum and the 4th minimum and the feature of a shelf on the inner portion of the 4th maximum are very sensitive to small changes in the parameters. The models A–F, J and T in the parameter chart can be ruled out because the relative depth of the 5th and the 6th minimum contradicts with experiments, while the models, O, S, V and W, are unacceptable because the 6th minimum is too deep as compared with experiments. The model I can also be rejected because of the prominence of a shelf on the inner portion of the 4th maximum. The model U is unsatisfactory because the 7th and the 8th maximum are too faint. The models, G, H, L, M, N, P and Q, are regarded as acceptable fits, while the models, K and R, can be accepted as borderline fits. In Table III is given the comparison between the observed and the calculated intensity curve for the best model L. In Table IV

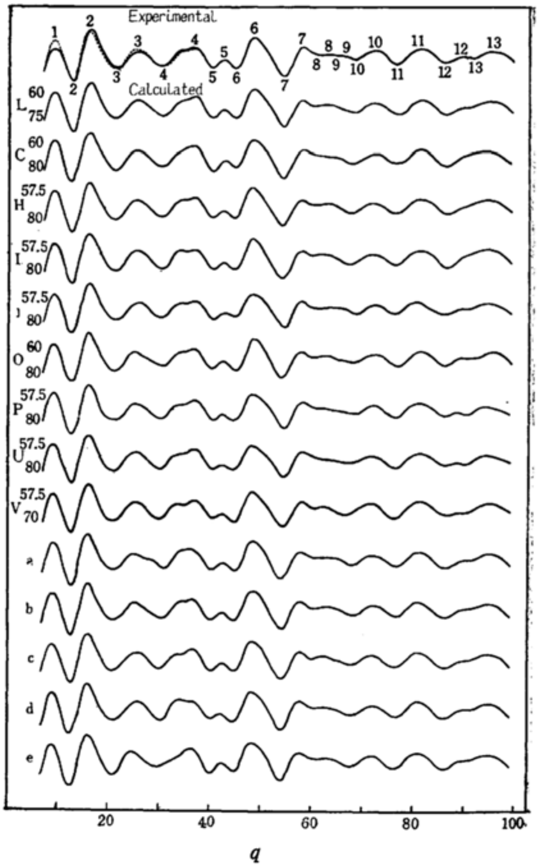

Fig. 5. Experimental and calculated intensity curves. In the experimental curve the dotted line indicates the correction for non-nuclear scatterings.

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

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

TABLE III

COMPARISON BETWEEN EXPERIMENTAL AND THEORETICAL INTENSITY CURVES

Max.	Min.	Peak position			Peak height		
		q_o	q_c	q_c/q_o	I_o	I_c	I_o/I_c
1		9.0	9.0	1.000	+1.30	+1.24	1.048
	2	12.5	12.5	1.000	−1.90	−1.98	0.960
2		16.0	16.0	1.000	+2.05	+2.00	1.025
	3	21.0	21.0	1.000	−0.98	−0.90	1.089
3		25.2	25.2	1.000	+0.61	+0.58	1.052
	4	30.2	30.2	1.000	−0.73	−0.71	1.028
4		36.6	36.7	1.003	+0.80	+0.82	0.976
	5	40.2	40.2	1.000	−0.85	−0.86	0.988
5		42.5	42.5	1.000	−0.18	−0.20	0.900
	6	44.8	44.8	1.000	−1.00	−0.93	1.075
6		48.3	48.4	1.002	+1.62	+1.51	1.073
	7	54.3	54.2	0.998	−1.52	−1.57	0.968
7		58.0	57.8	0.997	+0.78	+0.67	1.164
	8	61.4	60.6	(0.987)	+0.15	+0.05	(3.000)
8		63.4	62.4	(0.984)	+0.24	+0.26	(0.923)
9		66.2	65.5	(0.989)	+0.07	−0.05	(——)
	10	68.5	68.2	0.996	−0.26	−0.42	0.619
10		72.1	72.2	1.001	+0.52	+0.37	1.405
	11	76.5	76.7	1.003	−0.52	−0.55	0.982
11		81.1	81.2	1.001	+0.60	+0.65	0.923
	12	86.2	86.2	1.000	−0.54	−0.65	0.831
12		89.5	89.5	1.000	−0.03	0.00	(——)
13		95.4	95.0	0.996	+0.45	+0.50	0.900
Average				1.000			1.005
Average deviation				0.001			0.096

TABLE IV

DISTANCES OBTAINED FROM q_c/q_o VALUES

(THE DISTANCES ARE GIVEN IN Å UNITS)

Acceptable models	Average q_c/q_o	Average deviation	C—F$_1$	C—F$_2$	C—Cl$_1$	C—Cl$_2$	C—C
L_{75}^{60}	1.000	0.001	1.38_0	1.33_0	1.74_5	1.76_0	1.54_0
N_{70}^{60}	0.999	0.003	1.37_9	1.32_9	1.76_8	1.74_3	1.53_8
$K_{80}^{57.5}$	1.001	0.003	1.38_1	1.33_1	1.72_6	1.77_1	1.54_1
$G_{80}^{57.5}$	0.999	0.002	1.36_3	1.33_8	1.75_4	1.75_4	1.53_9
$H_{80}^{57.5}$	0.999	0.003	1.36_2	1.33_7	1.76_8	1.74_6	1.53_8
$P_{80}^{57.5}$	1.000	0.003	1.39_5	1.32_0	1.72_5	1.77_0	1.54_0
Q_{75}^{60}	0.999	0.003	1.39_4	1.31_9	1.74_3	1.75_8	1.53_9
Most probable value			1.37_9	1.32_9	1.74_7	1.75_8	1.53_9

are listed the mean values of the q_c/q_o ratio for these acceptable models as well as the molecular parameters calculated therefrom. The accepted values of these parameters and the limits of errors are as follows:

$$\text{C—F}_1=1.37_9\pm0.02_1\text{Å} \quad \text{C—F}_2=1.32_9\pm0.01_4\text{Å}$$

$$\text{C—Cl}_1=1.74_7\pm0.02_7\text{Å} \quad \text{C—Cl}_2=1.75_8\pm0.02_0\text{Å}$$

With respect to the parameter N_g the models for $N_g=100$ per cent were all unsatisfactory because the positions of the 3rd maximum and the 4th minimum did not agree with experiments. This discrepancy could not be removed without taking into account the coexistence of the C_s form. Therefore, the existence of the C_s form is definitly concluded from the diffraction data. From the acceptable domains estimated for acceptable models in the $\rho_F-\rho_{Cl}$ parameter chart, the limits of errors for the N_g and ϕ parameters were determined as follows:

$$N_g=76\pm7 \text{ per cent} \quad \phi=59.5\pm3.5°$$

These values coincide with the results from the analysis of the RD curve.

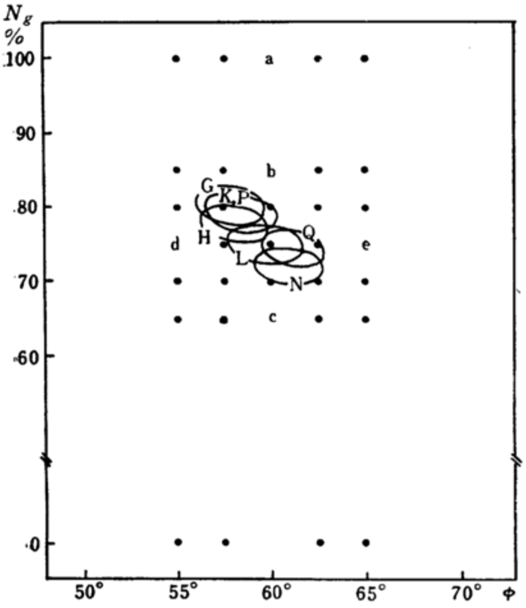

Fig. 6. Parameter chart for N_g and ϕ. The positions of the small letters and dots indicate the parameters of the models for which intensity curves were computed. The areas enclosed in the curved lines roughly indicate the acceptable regions for the models represented by the capital letters, which correspond to the positions in the $\rho_{Cl}-\rho_F$ parameter chart. The theoretical intensity curves corresponding to the positions indicated by the small letters are reproduced in Fig. 5.

Discussion of the Results

The shortening of the C—F bond distance found in $CF_2Cl—CF_2Cl$[3] is also revealed in this molecule. It is concluded that the C—F bond distance in a $-CF_2Cl$ group is different from that in a $-CFCl_2$ group. Moreover, the values of these distances are almost the same as those found in CF_2Cl-CF_2Cl and $CFCl_2-CFCl_2$. It implies that the structure of one half of the molecule scarcely affects the other half of the molecule. With respect to the C—Cl bond distances it appears that the similar difference in two halves of the molecule also exists, although great uncertainties of the data do not permit to draw a definite conclusion. From the analysis described in the preceding section, it was definitly concluded that there exist two rotational isomers, C_s and *gauche* forms for $CF_2Cl-CFCl_2$ molecules in the vapor state, the amount of the *gauche* form being 76±7 per cent. If the ratio of the vibrational and rotational partition functions for the C_s and the *gauche* form is assumed to be equal to unity, the energy difference, ΔE, between the isomers is calculated as 270±250 cal./mol. (the *gauche* form is more stable than the C_s form.) from diffraction data, in remarkable contrast to the value of 2900 cal./mol.[18,19] for $CH_2Cl-CHCl_2$. It appears that this lowering of energy difference arises mainly from the decrease in the difference of electrostatic interactions between the C_s and the *gauche* form due to the fluorine substitution, because the C—Cl bond moment is nearly equal to the C—F bond moment. The decrease in the difference of steric repulsion between the C_s and the *gauche* form, of course, should not be neglected, because the van der Waals' radius of a fluorine atom is larger than that of a hydrogen atom. However, the effect of the change in the steric interaction is less important for this lowering because it was reported[20] that the methyl substitution does not appreciably affect the energy differences in chlorinated ethanes.

In the case of 2-methylbutane, $CH_2(CH_3)-CH(CH_3)_2$, which has a similar skeletal structure to that of $CH_2Cl-CHCl_2$ but has a large difference in electrostatic interaction, the energy difference is reported by Sheppard and Szasz[21] to be almost zero. In this connection, it is interesting to mention that a large energy difference was not observed in a $CF_2Cl-CFCl_2$ molecule, in which the difference of electrostatic interactions decreases.

The azimuthal angle of the *gauche* form was determined to be 59.5° in contrast to the value of 70° in $CH_2Cl-CHCl_2$[22]. This change in the equilibrium position of the *gauche* form seems to have some relation to the lowering of the energy difference.

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[18] J. R. Thomas and W. D. Gwinn, *J. Am. Chem. Soc.*, **71**, 2785 (1949).

[19] K. Kuratani and S. Mizushima, *J. Chem. Phys.* **22**, 1403 (1954).

[20] I. Miyagawa, *J. Chem. Soc. Japan, Pure Chem. Sec.*, (*Nippon Kagaku Zassi*), **75**, 1162 (1954).

[21] N. Sheppard and G. J. Szasz, *J. Chem. Phys.*, **18**, 145 (1950).

[22] A. Turkevich and J. Y. Beach, *J. Am. Chem. Soc.*, **61**, 3127 (1939).

The result in this investigation is consistent with the conclusion reached by Mizushima, Morino and Shimanouchi[23] that the most important force in dtermining stable configurations of rotational isomers is the steric repulsion and that the electrostatic force plays an important role in determining the energy difference between the rotational isomers because the steric repulsion may become of the same order of magnitude as the electrostatic force in the stable configurations.

Summary

The molecular structure of 1,1,2-trifluoro-1,2,2-trichloroethane was investigated by means of the sector-microphotometer method of electron diffraction. The existence of the two isomeric forms, C_s and *gauche* was ascertained and the amount of the *gauche* form was found to be 76±7 per cent at 20°C. This corresponds to the energy difference of 270±250 cal./mol., the *gauche* form being more stable than the C_s form. The interatomic distances were determined as follows: $C—F_1=1.37_9±0.02_1$Å, $C—F_2=1.32_9±0.01_4$Å, $C—Cl_1=1.74_7±0.02_7$Å, $C—Cl_2=1.75_8±0.02_0$Å and the equilibrium angle of the *gauche* form is 59.5±3.5°, where the C—C bond distance and the bond angles were assumed to be equal to the value of $CF_2Cl–CF_2Cl$ and $CFCl_2–CFCl_2$ molecules, which have already been investigated by the present author.

The diffraction patterns and the microphotometer traces were taken by using apparatuses in Nagoya University. The author wishes to express his sincere gratitude to Professor M. Kubo, Professor R. Uyeda and Dr. Kimura for giving him facility to use the apparatuses and for their valuable advice. Thanks are also due to Dr. S. Shibata, Mr. H. Morimoto and Mr. K. Kimura of Nagoya University for their friendly assistance, and to Mr. K. Kuchitsu of the University of Tokyo for his help in calculating theoretical intensities by means of a punched card machine. Further, the author is much indebted to Professor Y. Morino of the University of Tokyo for his helpful criticism on this investigation.

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[23] S. Mizushima, Y. Morino and T. Shimanouchi, *J. Phys. Chem.*, **56**, 324 (1952).