Molecular Structure and Rotational Isomerism of Some Fluorochloroethanes

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The problem of rotational isomerism in chlorinated ethanes has been well elucidated by a number of investigators from various points of view. In the series of CH_2Cl-CH_2Cl, $CHCl_2$-CH_2Cl and $CHCl_2$-$CHCl_2$, the energy differences between the *trans* (or C_s) and the *gauche* forms are expected to be almost equal, from simple considerations on the interaction between non-bonded atoms. Contrary to this expectation, the experimental evidence shows that there are remarkable variations in the energy differences in these three compounds: the energy difference for CH_2Cl-CH_2Cl is reported to be 1.0$\sim$1.3 kcal./mol. by many investigators[1-4], that for $CHCl_2$-CH_2Cl is 2.9kcal./mol.[5,6] and that for $CHCl_2$-$CHCl_2$ is nearly 0 kcal./mol.[5,7], these data being evaluated in the vapor state.

Miyagawa[8] suggested that this variation of the energy difference for these three compounds arises from the induction effect and the difference in bond angles. Kreevoy and Mason gave in their recent paper[9] the same explanation for this experimental result. Miyagawa[10] also reported that the substitution of a hydrogen atom in chloroethanes with a methyl group having a van der Waals' radius almost equal to that of chlorine atom gave no appreciable decrease of the energy difference between the isomers. This fact stimulates the investigation of the effect of fluorine substitution which introduces the C—F bond moment that is almost equal to the C—Cl bond moment in contrast to the methyl substitution which introduces inappreciable change in electrostatic interaction.

Furthermore, the general applicability and the merits of various potential functions[8,9] that have recently been proposed can not be criticized until comprehensive data on the molecular parameters are available. Therefore, it is desirable to carry out a study on the molecular structure and the rotational isomerism of some fluorochloroethanes by electron diffraction which will give the data for the energy difference and the azimuthal angle of the *gauche* form in addition to other molecular parameters.

The present writer has undertaken studies on the molecular structure of CF_2Cl-CF_2Cl, $CFCl_2$-CF_2Cl and $CFCl_2$-$CFCl_2$ in order to find the effect of fluorine substitution on the energy difference between the isomers and on the bond distances.

Apparatus. — In earler investigations, the molecular scattering term required for the analysis of molecular structures was estimated visually from the total scattering which was the supperposition of small oscillation corresponding to the molecular term and the steeply falling background corresponding to atomic and incoherent scatterings, because the background fell off very rapidly with an increasing scattering angle so that it was difficult to record and measure the pattern accurately. Therefore, the visual method may essentially be free from a large error in the estimation of intensities. As a matter of fact, there is a limit in the accuracy of the molecular parameters determined by the visual method; moreover this method is not sufficiently reliable to provide solutions for such a complicated problem as that of rotational isomerism.

This difficulty has been overcome by the use of a rotating sector to compensate for the sharp drop in intensity by screening electrons appropriately before they reach the photographic emulsion used to record the pattern, and by the measurement of the resulting diffraction patterns with a recording microphotometer. The sector-microphotometer method has been proposed independently by C. Finbak[11] and by P. Debye[12] and has been developed by the

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1) I. Watanabe, S. Mizushima and Y. Morino, *Sci. Papers Inst. Phys. Chem. Research (Tokyo)*, **39**, 401 (1942).

2) T. Shimanouchi, H. Tsuruta and S. Mizushima, ibid., **42**, 51 (1944).

3) H. J. Bernstein, *J. Chem. Phys.*, **17**, 258 (1949).

4) W. D. Gwinn and K. S. Pitzer, ibid., **16**, 303 (1948).

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

7) K. Naito, *Repts. Osaka Ind. Research Inst.*, (*Osaka Kogyogijutsu Shikenjo Kiho*), **8**, 1 (1957).

8) I. Miyagawa, *J. Chem. Soc. Japan. Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **75**, 1169, 1173, 1177 (1954).

9) M. M. Kreevoy and E. A. Mason, *J. Am. Chem. Soc.*, **79**, 4581 (1957).

10) I. Miyagawa, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **75**, 1162 (1954).

11) C. Finbak, *Avhandl. Norske Videnskaps-Akad. Oslo I. Mat.-Naturv. Kl.* **13**, (1937).

12) P. P. Debye, *Physik. Z.*, **40**, 404 (1939).

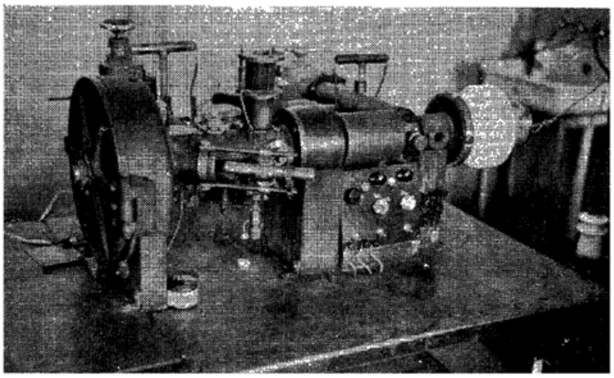

Fig. 1. External appearance of an electron diffraction unit.

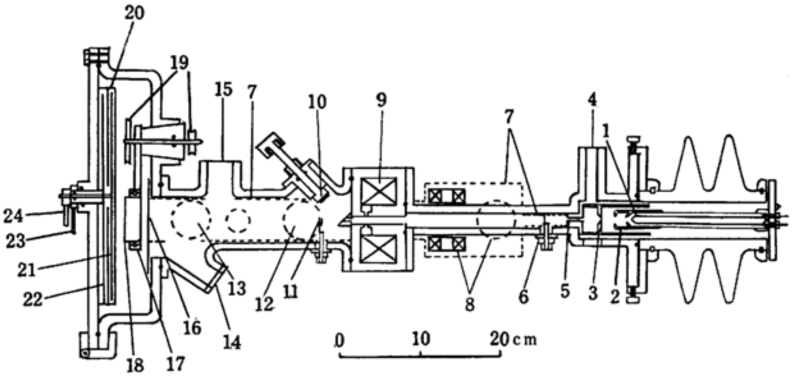

Fig. 2. Sectional drawing of an electron diffraction unit.
1. filament, 2. Trichter, 3. anode, 4. to pump, 5. diaphragm, 6. slit, 7. shield case made of permalloy, 8. Helmholz coil, 9. magnetic lens, 10. stop valve, 11. slit, 12, 13. port for specimen injection, 14. window, 15. to pump, 16. fluorescent screen, 17. ball bearing, 18. sector, 19. pulley for rotating the sector, 20. cassette, 21. fluorescent screen, 22. photographic plate, 23. handle for rotating photographic plates, 24. handle for rotating fluorescent screen.

Norwegian school[13]. Several laboratories[13-18] now use this method in electron diffraction investigation on molecular structures. In our country, the first apparatus having a rotating sector was constructed by Ino[19] and applied to thin amorphous films of a high polymer. The apparatus[20] used in this study was designed and constructed after the example of Ino's apparatus and some device was made for the treatment of gaseous samples.

Figs. 1 and 2 show the external appearance and the sectional drawing of the electron diffraction unit, respectively. It consists of four parts: an electron gun, a collimating system, a specimen chamber and a diffraction chamber. Cylinders made of permalloy were used for shielding electron beams from the external magnetic field. The electron gun was of a hot cathode type, consisting of a filament, a Trichter[21] biasing cup and an anode. The divergent beam from the gun was focused on the plane of photographic plates by a single magnetic lens. The direction of the beam was precisely controlled and adjusted to the center of the sector by means of two pairs of Helmholtz coils which are set at a right angle to each other. Two ports are provided for introducing specimens into the electron beam, one at 125 mm. and the other at 285 mm. from the photographic plate. The shorter distance is suitable for studies on moderate and wide-angle scatterings, $20 < q < 105$, and the longer distance

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13) C. Finbak, O. Hassel and B. Ottar, *Arch. Math. Naturvidenskap.*, **44**, No. 13 (1941); O. Hassel and H. Viervoll, *Acta Chem. Scand.*, 1, 149 (1947); O. Bastiansen, *Det 8. Nordiske Kjemikermfte. Beretning og Foredrag.*, **1954**, 139; O. Bastiansen, O. Hassel and E. Risberg, *Acta Chem. Scand.*, **9**, 232 (1955).

14) I. L. Karle and J. Karle, *J. Chem. Phys.*, **17**, 1052 (1949); J. Karle and I. L. Karle, ibid., **18**, 957 (1950); I. L. Karle and J. Karle, ibid., **18**, 963 (1950).

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16) L. O. Brockway and L. S. Bartell, *Rev. Sci. Instr.*, **25**, 569 (1954).

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19) T. Ino, *J. Phys. Soc. Japan*, **8**, 92 (1953).

20) Y. Morino, M. Kimura and M. Iwasaki, The Sixth Annual Meeting of the Chemical Society of Japan (1953).

21) K. H. Steigerwald, *Optik*, **5**, 459 (1949).

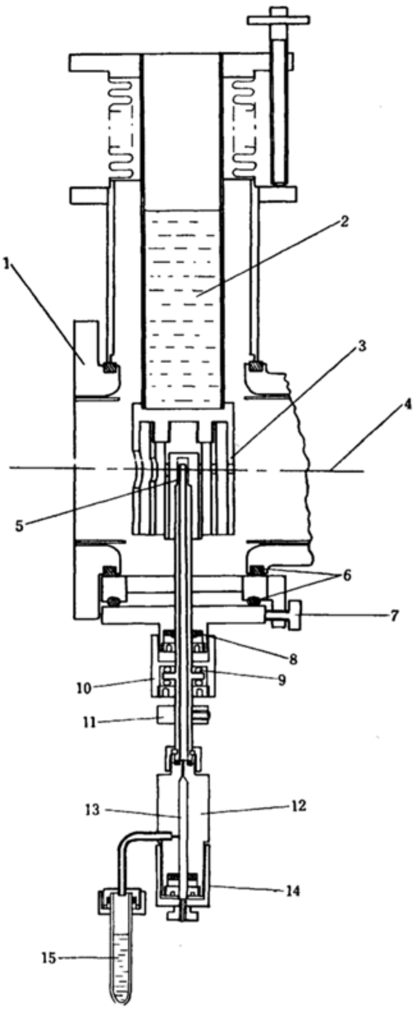

Fig. 3. Sectional drawing of a specimen injection system.
1. body of a diffraction unit, 2. liquid air, 3. cold trap, 4. electron beam, 5. nozzle, 6. rubber packing, 7. cross leader, 8. Wilson seal, 9. ball, 10. screw for adjusting the position of the nozzle, 11. nob, 12. needle valve, 13. needle, 14. screw for adjusting the inlet pressure, 15. sample.

is useful for examination of small angle scattering, $7 < q < 45$. The system of specimen injection is shown in Fig. 3 and the nozzle of a drum type is used. At first sight, it seems likely that in the nozzle of this type the spreading of samples is rather large and so the multiple and extraneous scatterings are serious. However, in practical use, a nozzle of this type makes it possible to take very clean diffraction patterns in lower inlet pressure of gas than that in the case of a nozzle of the ordinary type. Even if the inlet pressure of gas is sufficiently low and the cold trap is used, the diffraction patterns obtained have an index of resolution of 0.95～1.00; 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 0.95～1.00 times that given by theory for a perfect pattern. The inlet gas pressure can precisely be controlled by a needle valve having a mildly tapered needle. The spreading gas is caught by using the cold trap which consists of three-fold concentric cylinders. The stop valve which is set behind the magnetic lens permits the electron gun to be isolated from the other parts of the apparatus and to keep it evacuated in placing photographic plates as well as in altering the nozzle-to-plate distance. The wavelength of the electron beam is determined by means of a gold foil attached to the nozzle. The sector which has a spiral form with an angular opening increasing as the square of the radius[22] is provided because this form is somewhat more profitable than the heart form with respect to the accuracy of figuring and finish. The sector is mounted on the inner race of a ball bearing of phosphor bronze, which is rotated by a power supply introduced into the vacuum space through a Wilson seal and transmitted by a pulley and a phosphor bronze wire. The fluorescent screen placed in front of the sector assembly makes it possible to observe the diffraction patterns in their innate state without replacing the sector. Moreover, it serves as a shutter of the electron beam.

The experimental procedure and the method for deriving the molecular scattering intensity from diffraction data has been already described in previous papers[23-25].

Results

The detailed description of the analysis has already been reported in this Bulletin[23-25]. Only the results are briefly described in this paper.

The experimental and the theoretical intensity curves are reproduced in Fig. 4, and the radial distribution curves derived from the experimental intensities are shown in Fig. 5. The molecular parameters obtained by the radial and the correlation method are listed in Tables I and II. In all cases, the analyses were made on the assumption that the structural frame of molecules does not change with rotation about the C—C bond. In the case of a $CF_2Cl—CFCl_2$ molecule, the C—C distance and the bond angles for the two halves of the molecule were assumed to be equal to those of CF_2Cl-CF_2Cl and $CFCl_2-CFCl_2$, respectively.

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[22] At present, an r^3-sector constructed by S. Shibata is available as well as an r^2-sector. S. Shibata, Symposium on the X-ray and electron diffraction held in Osaka City University, Nov. 1956.

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

[24] M. Iwasaki, ibid. **31**, 1071 (1958).

[25] M. Iwasaki, ibid. **32**, 194 (1959).

TABLE I

THE MOLECULAR PARAMETERS FOR CF_2Cl-CF_2Cl, $CFCl_2$-CF_2Cl AND $CFCl_2$-$CFCl_2$

	CF_2Cl-CF_2Cl	$CFCl_2$-CF_2Cl	$CFCl_2$-$CFCl_2$
C—F(Å)	$1.33_0 \pm 0.01_5$	$1.32_9 \pm 0.01_4$ $1.37_9 \pm 0.02_4$	1.38 ± 0.02
C—Cl(Å)	$1.74_5 \pm 0.01_5$	$1.74_7 \pm 0.02_7$ $1.75_8 \pm 0.02_0$	1.76 ± 0.01
C—C(Å)	1.54 ± 0.04	1.53_9(*)	1.54 ± 0.06
∠CCCl	112 ±1.5°	112°(*) 112°(*)	112 ±2°
∠CCF	108 ±1.5°	108°(*) 107°05′(*)	107°05′
∠FCCl	110 ±1°	110°(*) 107.5°(*)	107.5±1.5°
∠FCF	108°44′	108°44′(*)	
∠ClCCl		110.5°(*)	110.5±1°

(*): Assumed

TABLE II

OBSERVED MEAN AMPLITUDES FOR CF_2Cl-CF_2Cl, $CFCl_2$-CF_2Cl AND $CFCl_2$-$CFCl_2$

	CF_2Cl-CF_2Cl	$CFCl_2$-CF_2Cl	$CFCl_2$-$CFCl_2$
C—F	0.052Å	0.055_5Å	0.064Å
C—Cl	0.061	0.054_0	0.062
C—C	0.045	0.041_7	——
$(F\cdots Cl)_t$	0.062	0.063_8	0.070
$(Cl\cdots Cl)_t$	0.088	0.069_5	0.081

The mean amplitudes were not determined except the values listed in Table II and the values estimated from the spectroscopic data and other electron diffraction data were used throughout these analyses.

The energy difference between the rotational isomers and the azimuthal angles of the *gauche* form in these three molecules are listed in Table III and the stable configurations are shown in Fig. 6. In the case of the CF_2Cl-$CFCl_2$ molecule, the configuration having the C_s symmetry is called the C_s form and that having no symmetry the *gauche* form as shown in Fig. 6. In all cases, the ***trans*** (or C_s) form was assumed to possess the C_{2h} (or C_s) symmetry but the azimuthal angle of

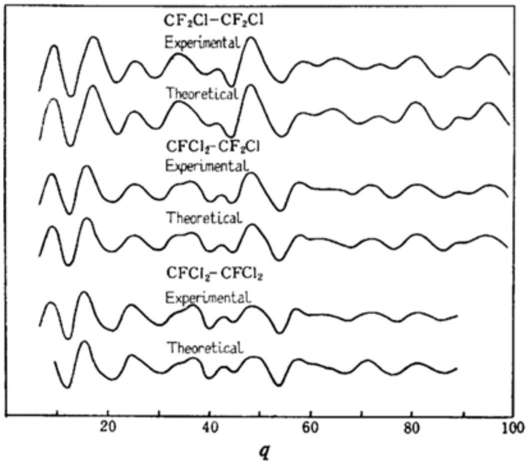

Fig. 4. Experimental and theoretical intensity curves.

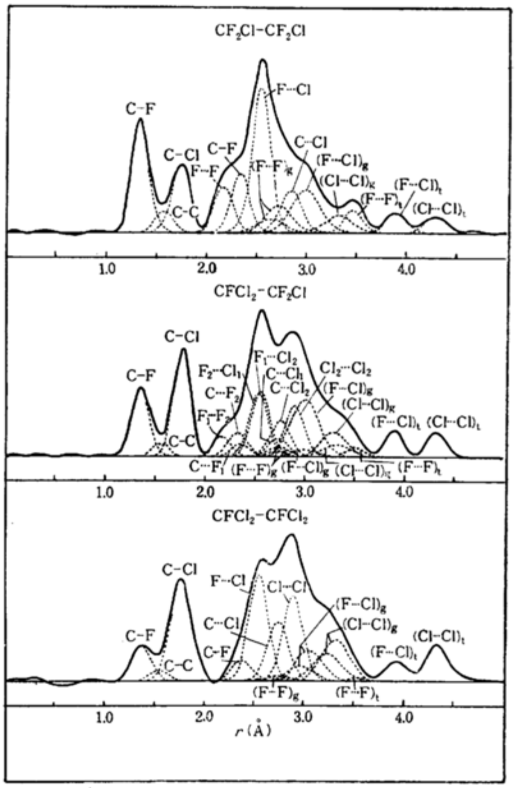

Fig. 5. Radial distribution curves.

TABLE III

THE ENERGY DIFFERENCE BETWEEN THE ROTATIONAL ISOMERS AND THE AZIMUTHAL ANGLE OF THE *GAUCHE* FORM FOR CF_2Cl-CF_2Cl, $CFCl_2$-CF_2Cl AND $CFCl_2$-$CFCl_2$

Molecules	Stable form	$N_g(\%)$	ΔE (cal./mol.)	Azimuthal angle of the *gauche* form
CF_2Cl-CF_2Cl	*trans* (C_{2h})	48± 5 (10°C)	440±110	62.5±3° (Cl-C-C-Cl)
$CFCl_2$-CF_2Cl	*gauche* (C_1)	76± 7 (20°C)	−270±250	59.5±3.5° (Cl-C-C-Cl)
$CFCl_2$-$CFCl_2$	*trans* (C_{2h})	55±10 (15°C)	280±240	59 ±4° (F-C-C-F)

N_g: Amount of the *gauche* form.

ΔE: Energy difference between the isomers. $\Delta E = E_g - E_t$ (or E_{C_s})

the *gauche* form was taken as an unknown parameter. The amounts of the rotational isomers were obtained from the area under the radial distribution peaks by using the successive approximation and further confirmation was made by analyzing the small angle scattering $(20 < q < 40)$ that was precisely measured by use of the long camera length. The azimuthal angle of the *gauche* form was also determined by the analysis of the radial distribution curve and the small angle scattering $(20 < q < 40)$.

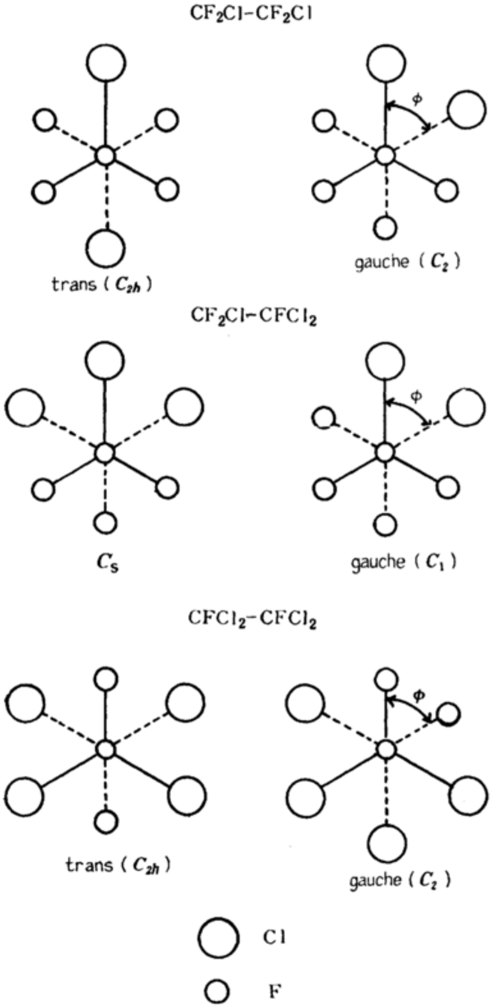

Fig. 6. Stable configurations.

Discussion

Bond Distances and Bond Angles.—The shortening of the C—X bond (X=halogen or carbon atom) by the substitution of hydrogen atoms in H_3C—X compounds with fluorine atoms was a historical problem which has been stimulating many investigators working in the field of electron diffraction and microwave spectroscopy. Brockway and Livingston[26] have first reported this shortening for many fluorinated hydrocarbons from the results of visual electron diffraction. On the other hand, Bauer[27] doubted whether or not this shortening was real, because of the great ambiguity inherent to visual electron diffraction. Thereafter, the development of microwave spectroscopy and the sector-microphotometer method of electron diffraction revealed that this shortening was real in the case of carbon-halogen bonds, although the magnitude of this shortening was somewhat smaller than that reported by Brockway and Livingston.

In the series in question, it was shown that the C—F bond distance decreased with the number of fluorine atoms attached to one and the same carbon atom, i.e., in a —$CFCl_2$ group the C—F bond distance is 1.38Å and in a —CF_2Cl group it is 1.33Å. These results coincide with the results of other organic fluorine compounds as shown in Table IV. The value of 1.38Å for $CFCl_2$-$CFCl_2$ coincides with those of the groups having a single fluorine atom attached to one and the same carbon atom. The value of 1.33_0Å for CF_2Cl-CF_2Cl seems to be slightly shorter than that for the group having two fluorine atoms attached to one and the same carbon atom,

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[26] L. O. Brockway and R. Livingston, *U. S. Naval Research Lab. Project M-510, Report No. 547.1. XA C-R-1080, A-3786.*

[27] S. H. Bauer, *U. S. Atomic Energy Com. Report, MDDC* 1494 (1947).

TABLE IV

THE MOLECULAR STRUCTURES OF SOME FLUORINATED HYDROCARBONS

Compounds	C—F(Å)	C—Cl(Å)	Other structure parameters	Method	Ref.
CH_3F	1.385		∠HCF=110°0′	MW	a
CH_2ClF	1.378±0.006	1.759±0.003	∠FCCl=110°01′±2′	MW	b
$CHCl_2F$	1.41 ±0.03	1.73 ±0.04	∠ClCCl=112°±2°, ∠FCCl=10.9°±2°	V	c
CCl_3F	1.40 ±0.04	1.76 ±0.02	∠ClCCl=111.5°±1°, ∠FCCl=107.5°±1°	V	c
$C(CH_3)_3F$	1.38 ±0.02		∠CCF=108°±1.5°	S	d
CH_3CH_2F	1.375		∠CCF=109°28′ (assumed)	MW	e
CH_2F_2	1.358±0.001		∠FCF=108°17′±6′	MW	f
$CHClF_2$	1.36 ±0.03	1.73 ±0.03	∠FCF=110.5°±1°, ∠FCCl=110.5°±1°	V	c
CCl_2F_2	1.35 ±0.03	1.74 ±0.03	∠FCF=109°±2°, ∠ClCCl=113°±2°	V	c
	1.33_5 ±0.02	1.77_5 ±0.02	∠FCF=109.5°±3°, ∠ClCCl=108.5°±2°	V	g
CHF_3	1.332±0.008		∠FCF=108°48′±45′	MW	h
$CClF_3$	1.328±0.002	1.751±0.004	∠FCF=108.6°±0.4°	S	i
	1.328±0.002	1.748±0.009	∠FCF=108.6°±0.4° (assumed)	MW	i
CH_3CF_3	1.335±0.005		C—C=1.530±0.005, ∠CCF=111°2′±17′	MW	j
CF_3CF_3	1.32 ±0.01		∠CCF=109.5°±1.5°	S	k
CF_4	1.323±0.005			S	l

MW: microwave, V: visual, S: sector

a) O. R. Gillam, H. D. Edwards and W. Gordy, *Phys. Rev.*, **75**, 1014 (1949).
b) N. Muller, *J. Am. Chem. Soc.*, **75**, 860 (1954).
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) D. R. Lide, *J. Am. Chem, Soc.*, **74**, 3548 (1952).
g) R. L. Livingston and R. H. Lyon, *J. Chem. Phys.*, **24**, 1283 (1956).
h) S. N. Ghosh, R. Trambarulo and W. Gordy, ibid., **20**, 605 (1952).
i) L. S. Bartell and L. O. Brockway, ibid., **23**, 1860 (1955).
j) W. F. Edgell, ibid., **16**, 1002 (1948).
k) D. A. Swick and I. L. Karle, ibid., **23**, 1499 (1955).
l) L. O. Brockway, C. G. Thornton and L. S. Bartell, Am. Chem. Soc. Meeting, Los Angeles, California, March 1953.

but the difference is inappreciable in view of errors involved in experiments.

On the other hand, although the inaccuracies of the data do not permit us to draw a definite conclusion, it appears to be likely that the C—Cl distance also decreases with the number of fluorine atoms. Recently, Livingston and Lyon[28] reported a slightly greater value 1.77_5Å for the C—Cl distance in CF_2Cl_2 in disagreement with the present value, although the difference is within experimental errors. Their result seems to be related to the fact that the ClCCl bond angle 108.5°, obtained by them, is slightly shorter than the tetrahedral value, 109.5°. In this connection, it is desirable to determine the C—Cl distance in CF_2Cl_2 by the sector-microphotometer method or the microwave spectroscopy. The value of the C—Cl distance determined for the extreme case of a $CClF_3$ molecule in which three atoms except one chlorine atom were replaced by fluorine atoms was reported to be 1.748Å[29,30] from the microwave spectroscopy and 1.751Å[30] from the sector-microphotometer method of electron diffraction. In the case of a CF_2Cl-CF_2Cl molecule having two fluorine atoms attached to one and the same carbon atom, the C—Cl bond distance was found to be slightly shorter than the extreme value, the difference being also within experimental errors.

With regard to the C—C bond distance, although a definite conclusion could not be drawn because of the greater ambiguity of the data, experimental results could be explained by the normal distance of the C—C bond. It is not likely that such a

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[28] R. L. Livingston and D. H. Lyon, *J. Chem. Phys.*, **24**, 1283 (1956).

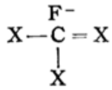
[29] D. K. Coles and R.H. Hughes, *Phys. Rev.*, **76**, 858(1949).

[30] L. S. Bartell and L. O. Brockway, *J. Chem. Phys.*, **23**, 1860 (1955).

large shortening as reported in earlier investigations was realized in the present molecules.

With respect to bond angles, it is to be noted that the FCF angle is less than the tetrahedral value, in agreement with recent determinations on other fluorinated hydrocarbons. This is interesting together with the fact that the decrease in the FSiF angle from the tetrahedral value was also reported in the case of organosilicon compounds. For example, the FSiF angle is 108°17′±30′ for $SiHF_3$[31] and 107°56′ ±6′ for SiH_2F_2[32]. Other bond angles are also consistent with the values found in other related molecules.

Such a shortening of the carbon-halogen bond was originally explained by Pauling[33] by the assumption of resonance structures of the type



$$X-\overset{F^-}{\underset{X}{C}}=X^+ \quad (X=F \text{ or } Cl)$$

The fact that the C—F shortening is more marked than the C—Cl shortening is attributed to the great tendency of a fluorine atom to form double bonds. It is conceivable that the structures of this type can also contribute to the slight closing of the FCF angle because of the Coulomb attraction between F^- and F^+.

Rotational Isomerism.—From the present studies, it was definitly confirmed that there exist two isomers, the *trans* (or C_s) and the *gauche* forms, in the vapor state for the series of the molecules in question. As shown in Table III the energy differences were almost of the same magnitude and considerably small compared with the remarkable variation and large values (except $CHCl_2$—$CHCl_2$) observed in the series of chloroethane: CH_2Cl-CH_2Cl (1.2 kcal./mol.), $CHCl_2$-CH_2Cl (2.9 kcal./mol.) and $CHCl_2$-$CHCl_2$ (0 kcal./mol.). It is said that the internal rotation is subject mainly to the steric and electrostatic interactions. According to the replacement of a hydrogen atom with a fluorine atom, the nature of three atoms contained in two groups rotating against each other is more close together in both "steric" and "electrostatic" senses as compared with the case of chloroethanes. As a concequence of this circumstance, it is likely that the potential energy of the *trans* (or C_s) form becomes nearly equal to that of the *gauche* form. It was reported by Miyagawa[10] that the replacement of a hydrogen atom with a methyl group in chloroethanes gave no serious decrease of the energy difference between the isomers and did not affect the tendency of the change in the energy differences with the number of chlorine atoms substituted in the molecules, although a methyl group having almost the same van der Waals' radius as a chlorine atom was introduced. Moreover, a fluorine atom may be closer to a hydrogen atom in the magnitude of the steric interaction than a chlorine atom, because the potential barrier of CF_3-CF_3, 3.92 kcal./mol.[34] is close to that of CH_3-CH_3, 2.875 kcal./mol.[35] as compared with the value in CCl_3-CCl_3, 10.8 kcal./mol.[36]. Accordingly, the main factor contributing to this lowering of energy difference in fluorochloroethane is presumably due to the decrement of the electrostatic interaction rather than the steric interaction. In fact, it is well known that the bond moment of C—F is approximately equal to that of C—Cl.

From a simple assumption of the additivity of interaction energy and the constancy of the bond distances as well as bond angles, it is expected that the energy differences are all the same in the series of 1,2-di-, 1,1,2-tri- and 1,1,2,2-tetrasubstituted ethanes. However, the observed energy differences in chloroethanes were not the same and indicated a remarkable variation which was explained by the induction effect and the opening of the ClCCl bond angle[8] as described in foregoing section. In the series of chlorofluoroethanes, the changes of the energy difference caused by the effect of induction are very small and the ClCCl bond angles are close to the tetrahedral angle. As a result of this circumstance, it appears to be likely that the energy differences in the present series represent almost the same value.

From the theoretical side, many attempts have been made to predict the hindering potential for the internal rotation about single bonds, based on a simple model for interactions between non-bonded atoms or groups. Among a number of attempts, the treatments recently made with tolerable success by Miyagawa[8] and Mason

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[31] G. A. Heath, L. F. Thomas and J. Sheridan, *Trans. Faraday Soc.*, **50**, 779 (1954).

[32] V. W. Laurie, *J. Chem. Phys.*, **26**, 1359 (1957).

[33] L. Pauling, "*The Nature of the Chemical Bond*", Cornell University Press, Ithaca, N. Y., 1945, p. 235.

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TABLE V

OBSERVED AND CALCULATED ENERGY DIFFERENCES (kcal./mol.)

Molecule	ΔE_{obs}	ΔE_{e}	Lennard-Jones		Buckingham	
			ΔE_{s}	ΔE_{total}	ΔE_{s}	ΔE_{total}
CF_2Cl-CF_2Cl	0.44	0.15	−0.10 (0.00)	0.05 (0.15)	0.30	0.45
$CFCl_2$-CF_2Cl	−0.27	−0.17	0.15 (0.05)	−0.02 (−0.12)	−0.20	−0.37
$CFCl_2$-$CFCl_2$	0.28	0.15	−0.25 (−0.13)	−0.10 (0.02)	−0.05	0.10

$\Delta E = E_g - E_t$ (or E_{C_s})

TABLE VI

OBSERVED AND CALCULATED AZIMUTHAL ANGLE OF THE *GAUCHE* FORM

Molecule	ϕ_{obs}	ϕ_{calc}(I)	ϕ_{calc}(II)
CF_2Cl-CF_2Cl	117.5°	118° (119°)	116°
$CFCl_2$-CF_2Cl	122	123 (122)	124
$CFCl_2$-$CFCl_2$	121	120 (120)	118

ϕ_{calc}(I): Lennard-Jones

ϕ_{calc}(II): Buckingham

and Kreevoy[9] seem to be most promising. The former author used a Lennard-Jones type potential while the latter a modified Buckingham type potential for interatomic interactions.

In order to estimate quantitatively the energy differences, a similar treatment was applied to the present case. The Lennard-Jones type potential for fluorine-fluorine interaction was approximated by the following formula for neon-neon interaction[37],

$$V(\mathrm{F-F}) = 7.148\times10^4/r^{12} \\ -143.58\times r^6\ \text{kcal./mol.} \qquad (1)$$

The application of this formula leads to the value of 2.4 kcal./mol. for the potential barrier in CF_3-CF_3, minor terms due to dipole interaction being added. Though this value is somewhat smaller than the observed value 3.92 kcal./mol.[34], the two values seem to coincide roughly with each other for such approximate calculation. The formula applied by Miyagawa[8] to chlorinated ethanes with a fair success,

$$V(\mathrm{Cl-Cl}) = 2.332\times10^6/r^{12} \\ -2.180\times10^3/r^6\ \text{kcal./mol.} \qquad (2)$$

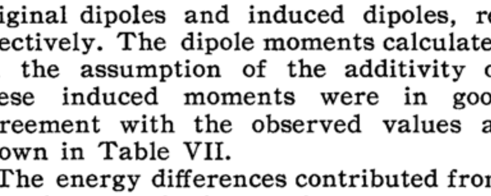
was adopted for chlorine-chlorine interaction. The expression for fluorine-chlorine interaction was derived through the method of averages proposed by Miyagawa[8] as follows:

$$V(\mathrm{F-Cl}) = 4.185\times10^5/r^{12} \\ -5.663\times10^2/r^6\ \text{kcal./mol.} \qquad (3)$$

As a result of the application of these formulas, the values listed in the 4th column of Table V were obtained for the energy differences due to steric interaction.

For the sake of comparison, the modified Buckingham type potential given by Mason and Kreevoy[9] was also applied to this problem. The results are listed in the 8th column of Table V.

With respect to the electrostatic interaction, dipole interactions were calculated taking into account of induction effects. For the sake of this computation, the following induced moment were estimated from the observed dipole moments in many chlorofluoroalkanes, assuming a vanishing C—H bond moment and the tetrahedral angle.



The thick and slender arrows indicate original dipoles and induced dipoles, respectively. The dipole moments calculated on the assumption of the additivity of these induced moments were in good agreement with the observed values as shown in Table VII.

The energy differences contributed from the electrostatic interactions were estimated using these dipoles and induced dipoles as shown in the 3rd column of Table V. In this calculation, the center of the dipole moment is located at seven-eighth of the bonded distance from the carbon atom. Total energy differences listed in the 6th and the 9th column of Table V approximately coincide with the observed

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TABLE VII

CALCULATED AND OBSERVED DIPOLE MOMENTS IN CHLOROFLUOROALKANES (VAPOR STATE)

Molecule	μ(calc.)	μ(obs.)	Ref.
CH_3F	1.81	1.81	a
CH_3Cl	1.87	1.87	b, c, d
CH_2F_2	1.97	1.96	e
CHF_3	1.61	1.62	f
		(1.64_5)	(g)
CH_2Cl_2	1.63	1.62	h
$CHCl_3$	0.97	0.95	i
		(1.02)	(j)
$CFCl_3$	0.44	0.45	k
CF_2Cl_2	0.52	0.51	k
		(0.55)	(l)
CF_3Cl	0.46	0.46	f
$CHFCl_2$	1.20	1.29	k
CHF_2Cl	1.41	1.39_6	k
CH_3CH_2F	1.90	1.92	a
CH_3CHF_2	2.28	2.24	m
CH_3CF_2Cl	2.16	2.14	n
CH_3CF_3	2.33	2.32	d
$(CH_3)_3CF$	2.05	2.05	o
CF_3CHF_2	1.53	1.54	f
CF_3CF_2Cl	0.51	0.52	f
CH_3CH_2Cl	1.96	2.03	p
CH_3CHCl_2	2.01	2.07	j
CH_3CCl_3	1.81	1.79	j
$(CH_3)_3CCl_3$	2.15	2.13	q
CH_2ClCCl_3	1.39	1.39	r
$CHCl_2CCl_3$	0.89	0.92	r
$(CH_2ClCH_2F)_g$	2.64 $(\phi=68°37')$	2.64	n
$(CHCl_2CHF_2)_g$	2.10 $(\phi=60°)$	2.10	n

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o) F. Andersen, J. R. Andersen, B. Bak, O. Bastiansen, E. Risberg and L. Smedvik, *J. Chem. Phys.*, **21**, 373 (1953).
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values. The modified Buckingham type potential seems to give somewhat better results. However, if two constants in Lennard-Jones type potential are adjusted so as to give observed potential barrier in CF_3-CF_3, the agreement between the calculated and observed energy differences becomes better as shown in the 7th column of Table V. The modified potential functions used in this calculation are as follows:

$$V(\mathrm{F—F}) = 12.729\times10^4/r^{12} - 2.5569\times10^2/r^6 \text{ kcal./mol.} \qquad (4)$$

$$V(\mathrm{F—Cl}) = 5.5839\times10^5/r^{12} - 7.5565\times10^2/r^6 \text{ kcal./mol.} \qquad (5)$$

It is to be noted that the azimuthal angles of the *gauche* forms calculated from these potential functions are in excellent agreement with observed values as shown in Table VI. In this calculation, the angle was measured from the *trans* (or C_s) position. This agreement may indicate that the potential functions used were fairly adequate.

In the above calculation, the effects of resonance arising from the substitution with fluorine atoms were not included explicitly. However, the changes of the geometry caused by resonance were considered to be implicitly taken into account by using the molecular parameters obtained from the electron diffraction. Furthermore, the changes of the charge distribution were also considered to be implicitly contained in the estimation of the induced moment as a result of ascribing the lowering of the dipole moment caused by resonance to that by induction.

From the foregoing consideration, it is concluded that the substitution of hydrogen atoms in chlorinated ethanes with fluorine atoms decreases the difference of the electrostatic interaction between the *trans* (or C_s) and the *gauche* form, and that as a consequence the energy differences in fluorochloroethanes decrease and become almost equal to one another irrespective of the number of chlorine atoms substituted in the molecules. This fact is consistent with the conclusion reached by Mizushima, Morino and Shimanouchi[38] that the most important force in determining stable configurations of rotational isomers is the steric repulsion, but the electrostatic force plays an important role in determining the energy difference between the rotational isomers, because in the stable configurations the steric repulsive force may become of the same order of magnitude as the electrostatic force.

TABLE VIII
THE ENERGY DIFFERENCES FOR RELATED COMPOUNDS (cal./mol.)

Molecule	X=H	X=F	Difference
CX_2Cl-CX_2Cl	1140	440	700
CX_2Cl-CX_2Br	1460	600	860
CX_2Br-CX_2Br	1700	945	755

As an example of the lowering of the energy difference caused by the fluorine substitution, one can point out the case of bromofluoroethanes studied by Kagarise et al.; that is, the energy difference in CF_2Br-CF_2Br is 945±50 cal./mol.[39] and that in CF_2Cl-CF_2Br is 600±200 cal./mol.[40] as compared with the value of 1700±40 cal./mol. for CH_2Br-CH_2Br[41] and 1460±30 cal./mol. for CH_2Br-CH_2Cl[41]. It is interesting to note that the lowering of energy difference caused by the fluorine substitution shows almost the same value as shown in Table VIII. In other words, this fact indicates that the electrostatic part of the energy difference in these molecules is of almost the same magnitude as 0.7~0.8 kcal./mol. This is caused by the fact that the C—F, C—Cl and C—Br bond moments are of almost the same magnitude. Moreover, the order of the energy differences in the series of CH_2Cl-CH_2Cl, CH_2Cl-CH_2Br and CH_2Br-CH_2Br does not change with the fluorine substitution and a considerable amount of the energy difference exists after the fluorine substitution. This fact indicates that the steric part cannot be neglected and its contribution becomes larger with the number of bromine substitutions.

Summary

In order to investigate the molecular structure and rotational isomerism, the electron diffraction camera having a rotating sector was designed and constructed and its application to some fluorochloroethanes was made successfully. The shortening of the C—F and the C—Cl bond by the substitution of atoms attached to one and the same carbon atom with other fluorine atoms was also revealed in fluorochloroethanes as well as fluorochloromethanes, although in the case of the C—Cl bond distance the inaccuracy of the data does not permit a definite conclusion to be drawn. It was definitly confirmed that there exist two rotational isomers, the *trans* (or C_s) and the *gauche* forms, in the vapor state for the molecules in question. The energy differences between the isomers and the azimuthal angles of the *gauche* form were determined and further discussed from the standpoint of intramolecular potential.

It was found that three fluorochloroethanes in question have almost equal and small energy differences in contrast to the remarkable variation in the case of chloroethanes. This is caused by the fluorine substitution which produces the decrease of the electrostatic part in the energy difference between the isomers.

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