# THE $r_s$ STRUCTURES OF PROPYL FLUORIDE AND DIFFERENCES IN STRUCTURES BETWEEN ROTATIONAL ISOMERS\*

MICHIRO HAYASHI and MASAHARU FUJITAKE

Department of Chemistry, Faculty of Science, Hiroshima University, Hagashi-sendamachi, Naka-ku, Hiroshima 730 (Japan)

(Received 26 June 1985)

## ABSTRACT

Microwave spectra of *trans* and *gauche* propyl fluoride and its isotopically substituted species have been measured. The  $r_s$  structures of the *trans* and *gauche* isomers of this molecule are determined from the observed moments of inertia. It is found that the CCC angle values are largely different between two isomers, while the CCF angle values stay unchanged. The  $r_s$  structures of ethyl fluorosilane and ethylmethyl sulfide are re-examined in order to compare the results with those of propyl fluoride. The differences in the structural parameter values between the rotational isomers are discussed for the present molecules and the analogous molecules such as ethanethiol and ethaneselenol.

#### INTRODUCTION

This investigation of the  $r_s$  structure of propyl fluoride was initiated due to our interest in the structures of ethyl fluorosilane [1], ethylmethyl sulfide [2, 3], ethanethiol [4, 5] and ethaneselenol [6].

For the *trans* and *gauche* isomers of ethylmethyl sulfide, it has been found that the CCS angle value of the *trans* isomer is much smaller than that of the *gauche* isomer. This fact is understood if the ethyl group tilts toward the lone pair electrons on the sulfur atom in a similar manner to the methyl group. However, the difference in the CCSi angle values between the *trans* and *gauche* isomers is also found for ethyl fluorosilane which has neither the lone pair electron nor the multiple bond responsible for the tilt of the ethyl group.

In order to compare the results with those of ethyl fluorosilane, we have determined the  $r_s$  structures of the *trans* and *gauche* isomers of propyl fluoride whose microwave spectra and  $r_0$  structures have already been reported by Hirota [7]. The microwave spectra of the two isomers of propyl fluoride and its isotopically substituted species were measured and the  $r_s$  structures were obtained from the observed moments of inertia.

The  $r_s$  structures of related molecules, such as ethyl fluorosilane and ethylmethyl sulfide, have already been reported by one of the present authors. However, the procedures and the formula used in the analyses were different

<sup>\*</sup>Dedicated to the memory of Prof. T. Shimanouchi.

from those used for propyl fluoride. The  $r_{\rm s}$  structures were re-evaluated for these molecules.

The structures are discussed by comparing the present structures of propyl fluoride with those of analogous molecules.

# EXPERIMENTAL

# Sample preparation

Samples of the normal and isotopic species were prepared by the following reactions with the appropriate commercial chemicals.

(1) Reactions from propyl alochol to propyl fluoride.

$$CH_{3}CH_{2}CH_{2}OH \xrightarrow{PBr_{3}} CH_{3}CH_{2}CH_{2}Br \xrightarrow{KF, 140^{\circ}C} CH_{3}CH_{2}CH_{2}F$$
(1)

(2) Reactions to prepare the appropriate isotopic propyl alcohol.

$$\overset{O}{\bigsqcup} \xrightarrow{\text{LiAID}_4} \overset{CH_2\text{DCH}_2\text{CH}_2\text{OH}} (2)$$

$$CH_{3}CH_{2}COCl \xrightarrow{\text{LiAlD}_{4}} CH_{3}CH_{2}CD_{2}OH$$
(3)

$$CH_{3}CH_{2}CHO \xrightarrow{\text{LiAlD}_{4}} CH_{3}CH_{2}CHDOH$$
(4)

$$CD_{3}I \xrightarrow{Mg} CD_{3}MgI \xrightarrow{20} CD_{3}CH_{2}CH_{2}OH$$
(5)

<sup>13</sup>CH<sub>3</sub>I and CHD<sub>2</sub>I were used for <sup>13</sup>CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>OH and CHD<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OH, respectively.

$$CH_{3}CD_{2}Br \xrightarrow{Mg}_{Et_{2}O} CH_{3}CD_{2}MgBr \xrightarrow{CH_{2}O}_{Et_{2}O} CH_{3}CD_{2}CH_{2}OH$$
(6)

 $CH_2O$  gas was generated from paraformaldehyde by pyrolysis.  $CH_3CHDBr$ , <sup>13</sup>C enriched ethyl bromide and <sup>13</sup>C enriched paraformaldehyde were used for  $CH_3CHDCH_2OH$ ,  $CH_3^{13}CH_2CH_2OH$  and  $CH_3CH_2^{13}CH_2OH$  species, respectively.

(3) Reactions to prepare the appropriate isotopic ethyl bromide.

$$CH_{3}CHO \xrightarrow{\text{LiAlD}_{4}} CH_{3}CHDOH \xrightarrow{\text{PBr}_{3}} CH_{3}CHDBr$$

$$CH_{3}COCl \xrightarrow{\text{LiAlD}_{4}} CH_{3}CD_{2}OH \xrightarrow{\text{PBr}_{3}} CH_{3}CD_{2}Br$$
(8)

For  $CH_3^{13}CH_2CH_2F$  and  $CH_3CH_2^{13}CH_2F$  species, the samples prepared contain about 50% of <sup>13</sup>C while the other samples contain about 90% of <sup>13</sup>C or D. The deuterated and <sup>13</sup>C enriched reagents used were purchased from Merck Sharp and Dohme, Canada.

## Spectral measurements

A conventional 100 kHz Stark modulation spectrometer was used for the measurements of the spectra at dry-ice temperature.

#### RESULTS

#### Microwave spectra

The gauche isomer of propyl fluoride is reported to be more stable than the trans isomer by 0.47 kcal mol<sup>-1</sup> and actually the microwave spectra of the gauche isomer are much more intense than those of the trans isomer. For the gauche isomer, the c-dipole component is much smaller than the aand b-components and a- and b-type transitions were measured. The asymmetry index  $\kappa$  is -0.845 and the observed frequencies of the transitions with  $J \leq 6$  and  $k_p \leq 2$  show appreciable amounts of centrifugal distortion contributions. Rotational constants were then obtained to fit about twenty-three observed transition frequencies with the rigid rotor and five van Eijck type centrifugal distortion terms [8].

For the *trans* isomer, the *c*-dipole component equals zero and the isomer is very close to the symmetric top molecule ( $\kappa = -0.980$ ). The observed *a*and *b*-type transitions exhibit very small centrifugal distortion contributions so that the rotational constants were obtained to fit the observed frequencies with  $J \leq 8$  and  $k_p \leq 1$  with the modified rigid rotor formula which contained the first term  $(d_J)$  of the centrifugal distortion terms.

The rotational constants are listed in Table 1. Details of the observed transition frequencies and the centrifugal distortion constants obtained have been deposited with the British Library Lending Division at Boston Spa, Yorkshire, U.K. as Supplementary Publication No. SUP 26293 (19 pages).

## r<sub>s</sub> Structure

The present data are sufficient to determine the  $r_s$  coordinates of the atoms in the molecule by the substitution method. The atom-labelling scheme of the two isomers is given in Fig. 1.

For the *trans* isomer, coordinate values of all the atoms in the molecule are not small, so the solutions of the Kraitchman equations are valid for all the coordinate values except for those of the fluorine atom.

For the gauche isomer, the  $x_c$  coordinate values of the hydrogen atoms  $H^4$ ,  $H^7$  and  $H^9$  are so small that the solutions of the Kraitchman equations are unreliable, while all the coordinate values of the hydrogen atoms  $H^3$ ,  $H^6$  and  $H^{10}$  which are equivalent atoms of  $H^4$ ,  $H^7$  and  $H^9$ , respectively, for the trans isomer, are not small and the solutions of the Kraitchman equations are reliable for these coordinates. Then, the assumptions  $r(CH^3) = r(CH^4)$ ,  $r(CH^6) = r(CH^7)$  and  $r(CH^9) = r(CH^{10})$  were used to fix the  $x_c$  coordinate values of the  $H^4$ ,  $H^6$  and  $H^9$  hydrogen atoms.

Rotational constants (MHz) of propyl fluoride<sup>a</sup>

	Position of substitution <sup>b</sup>	A	В	С
trans Isomer				
$1  \mathrm{CH_{3}CH_{2}CH_{2}F}$		26986.736(50)	3748.353(8)	3509.937(8)
2 <sup>13</sup> CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> F	2	26958,659(42)	3642.229(8)	3416.267(7)
3 CH <sub>3</sub> <sup>3</sup> CH <sub>2</sub> CH <sub>2</sub> F	5	26598.450(79)	3738.017(9)	3494.211(7)
4 CH <sub>3</sub> CH <sup>13</sup> CH <sub>2</sub> F	8	26631.088(40)	3742.150(7)	3498.410(7)
5 CD <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> F	1, 3, 4	23143.577(49)	3312.339(8)	3125.867(7)
6s-CH <sub>2</sub> DCH <sub>2</sub> CH <sub>2</sub> F	1	26507.972(85)	3544.744(12)	3323.837(10)
7 a-CH <sub>2</sub> DCH <sub>2</sub> CH <sub>2</sub> F	3	25215.391(50)	3608.703(9)	3389.139(8)
8 s-CHD, CH, CH, F	3, 4	23637.232(72)	3478.819(10)	3282.942(8)
9 a-CHD <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> F	1, 3	24721.109(55)	3424.903(10)	3218.737(9)
10 CH, CD, CH, F	6,7	22041.306(63)	3691.946(8)	3435.091(7)
11 CH, CHDCH, F	6	24253,290(38)	3723.163(7)	3468.980(7)
12 CH, CH, CD, F	9, 10	22121.072(43)	3694,428(7)	3440.885(7)
13 CH <sub>3</sub> CH <sub>2</sub> CHDF	9	24304,218(22)	3724.401(4)	3472.023(3)
gauche Isomer				
$1 \mathrm{CH_3CH_2CH_2F}$		14503.767(41)	5085.815(16)	4295.294(12)
2 <sup>13</sup> CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> F	2	14379.520(53)	4959.769(18)	4195.497(15)
3 CH <sub>3</sub> <sup>13</sup> CH <sub>2</sub> CH <sub>2</sub> F	5	14305.528(53)	5054.745(21)	4261.886(17)
4 CH <sub>3</sub> CH <sup>13</sup> CH <sub>2</sub> F	8	14318.819(29)	5059.673(11)	4267.052(9)
5 CD <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> F	1, 3, 4	12966.544(68)	4529.000(26)	3862.658(21)
6 CH <sub>2</sub> DCH <sub>2</sub> CH <sub>2</sub> F-1	1	14366.124(49)	4764.387(20)	4059.443(14)
7 CH <sub>2</sub> DCH <sub>2</sub> CH <sub>2</sub> F-3	3	13832.794(34)	4869.772(13)	4176.918(10)
8 CH <sub>2</sub> DCH <sub>2</sub> CH <sub>2</sub> F-4	4	13640.804(46)	5023.393(18)	4174.858(14)
9 CHD <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> F-1,3	1, 3	13700.012(89)	4577.738(43)	3959.828(26)
$10 \text{ CHD}_2 \text{CH}_2 \text{CH}_2 \text{F}-1,4$	1, 4	13547.216(99)	4711.376(42)	3955.037(30)
11 CHD <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> F-3,4	3, 4	13062.085(56)	4812.269(22)	4066.990(17)
$12 \mathrm{CH_3CD_2CH_2F}$	6,7	12778.303(34)	4901.867(13)	4130.334(10)
13 CH <sub>3</sub> CHDCH <sub>2</sub> F-6	6	13589.828(44)	4974.680(17)	4264.101(13)
14 CH <sub>3</sub> CHDCH <sub>2</sub> F-7	7	13563.426(45)	5010.519(17)	4157.441(14)
15 CH <sub>3</sub> CH <sub>2</sub> CD <sub>2</sub> F	9, 10	12911.854(48)	4894.921(19)	4142.795(14)
16 CH <sub>3</sub> CH <sub>2</sub> CHDF-9	9	13680.840(25)	5004.309(10)	4164.244(8)
17 CH <sub>3</sub> CH <sub>2</sub> CHDF-10	10	13626.945(34)	4973.028(13)	4270.673(10)

<sup>a</sup>Figures in parentheses indicate uncertainties attached to the last digit calculated from 2.5 times the standard deviation, <sup>b</sup>The atom identification number of the substituted atom by isotope (see Fig. 1).

The coordinate values of the fluorine atom were obtained by the first moment equations, using the values of the other atoms for both isomers.

When calculating the coordinate values using the Kraitchman equations, the remarks of Rudolph [9] were taken into consideration; that is, for the *trans* isomer, coordinate values of the atoms on the symmetry plane were used in the Kraitchman equation (eqn. (6) in Rudolph's paper). For every hydrogen coordinate, there are several pairs of the parent-isotopic species



Fig. 1. Atom-labelling scheme of *trans*- and *gauche*-propyl fluoride (X = C) and ethyl fluorosilane (X = Si).

useful to the solution of the Kraitchman equations, when an appropriate coordinate transformation to the principal axes system of the normal species is performed. The averages of the solutions obtained from the different pairs were used for the  $r_s$  coordinate values of these atoms [10]. Details of the solutions of the Kraitchman equations have also been deposited at B.L.L.D.

The coordinate values thus obtained are listed in Table 2, and the differences between the observed and calculated moments of inertia are given in Table 3.

The root mean square deviations (r.m.s.) of the observed and calculated moments of inertia for all the isotopic species used (13 species for the *trans* isomer and 17 species for the *gauche* isomer) are 0.4780 and 0.6816 amu Å<sup>2</sup> for the *trans* and *gauche* isomers, respectively. For the *gauche* isomer, the  $I_{ab}$ ,  $I_{ac}$  and  $I_{bc}$  values are -0.0770, 0.1119 and 0.0248 amu Å<sup>2</sup>, respectively.

Structural parameter values calculated from the coordinate values are listed in Table 4.

Atom no.		$\boldsymbol{x}_a$	<i>x</i> <sub>b</sub>	<i>x</i> <sub>c</sub>
trans Isom	er			
1	H(Hs)	-2.79107(19)	0.59283(80)	0.0
2	C	-1.99447(17)	-0.14278(236)	0.0
3, 4	H(Ha)	-2.12377(19)	-0.77260(50)	0.88439(47)
5	C	-0.61449(55)	0.52791(64)	0.0
6,7	Н	-0.49963(52)	1.16602(27)	0.88120(35)
8	С	0.47569(65)	-0.50418(62)	0.0
9,10	H	0.43034(48)	-1.13836(21)	0.89187(27)
11	$\mathbf{F}^{\mathbf{b}}$	1.72818(100)	0.12279(243)	0.0
gauche Ison	mer			
1	Н	2.57584(36)	-0.50821(172)	0.33578(195)
2	С	1.59117(28)	-0.54952(82)	-0.12122(365)
3	н	1.72836(45)	-0.54769(138)	-1.21425(62)
4	Н	1.08510(66)	-1.49714(59)	0.12258(3065) <sup>c</sup>
5	С	0.72664(62)	0.63532(72)	0.29870(154)
6	Н	0.60268(65)	0.66861(58)	1,38973(33)
7	Н	1.20448(35)	1.57878(39)	$0.00143(1414)^{c}$
8	С	-0.65083(50)	0.60231(55)	-0.30963(108)
9	Н	-1.25596(31)	1.47173(38)	$-0.02276(1132)^{c}$
10	Н	-0.58328(61)	0.55080(64)	-0.40377(27)
11	$\mathbf{F}^{\mathbf{b}}$	-1.33710(106)	-0.52571(162)	0.12545(711)

Atomic coordinates (Å)<sup>a</sup> of propyl fluoride

<sup>a</sup>Figures in parentheses indicate the uncertainties attached to the last digit. <sup>b</sup> Solved by the first moment equations. <sup>c</sup>Solved by the assumptions,  $r(CH^3) = r(CH^4)$ ,  $r(CH^6) = r(CH^7)$ , and  $r(CH^9) = r(CH^{10})$ , respectively.

## Re-evaluations of the $r_s$ structures of the analogous molecules

It is desirable that the  $r_s$  structures of the molecules analogous to propyl fluoride are evaluated in similar procedures when the structural parameter values are compared among the molecules. For ethyl fluorosilane and ethylmethyl sulfide, the rotational constants were determined so as to fit the observed frequencies with the rigid rotor and centrifugal distortion formulae of the Watson type  $(d_J, d_{JK}, d_K, d_{EJ}$  and  $d_{EK})$  in the previous papers. On the other hand, van Eijck [8] type centrifugal distortion formulae have been used in the present work. Since some of the five centrifugal terms were neglected in previous work, the rotational constants will be slightly shifted by the use of the van Eijck type expression. Furthermore, when calculating the coordinate values using the Kraitchman equations, the remarks of Rudolph [9] were not taken into consideration.

Therefore the  $r_s$  structures of ethyl fluorosilane and ethylmethyl sulfide were carefully re-evaluated.

	$I_a$	δIab	$I_b$	۶ <i>I</i> bb	$I_c$	$\delta I_c^{\mathbf{b}}$	P <sub>c</sub> c	$\Delta P_c^{\mathrm{d}}$
trans Isomer								
1 CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> F	18.72683(4)	0.14643	134.82615(29)	0.53981	143.98435(33)	0.60767	4.78431(33)	
2 <sup>13</sup> CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> F	18.74633(3)	0.14719	138.75459(31)	0.53911	147.93223(30)	0.60767	4.78435(32)	0.00003(64)
3 CH <sub>3</sub> <sup>3</sup> CH <sub>2</sub> CH <sub>2</sub> F	19.00021(6)	0.14466	135,19896(33)	0.53975	144.63237(29)	0.60767	4.78340(34)	-0.00092(66)
4 CH <sub>3</sub> CH <sub>1</sub> <sup>3</sup> CH <sub>2</sub> F	18.97692(3)	0.14538	135.04964(25)	-0.54002	144.45877(29)	0.60767	4.78389(29)	-0.00042(61)
5 CD <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> F	21.83656(5)	0.16285	152.57376(37)	0.54618	161.67547(36)	0.61247	6.36742(39)	1.58311(71)
6 s-CH2DCH2CH2F	19.06506(6)	0.15430	142.57052(48)	0.55267	152.04596(46)	0.60741	4.79481(50)	0.01049(83)
7 a-CH2DCH2CH2F	20.04236(4)	0.14989	140.04367(35)	0.53725	149.11634(35)	0.60810	5.48485(37)	0.70053(70)
8 s-CHD <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> F	21.38051(7)	0.15336	145.27229(42)	0.52861	153.93997(38)	0.60744	6.35641(43)	1.57210(75)
9 a-CHD,CH,CH,F	20.44310(5)	0.15852	147.55922(43)	0.55233	157.01065(44)	0.60994	5.49583(46)	0.71152(78)
10 CH <sub>3</sub> CD <sub>2</sub> CH <sub>2</sub> F	22.92859(7)	0.14334	136.88608(30)	0.54210	147.12158(30)	0.60797	6.34654(33)	1.56223(66)
11 CH <sub>3</sub> CHDCH <sub>2</sub> F	20.83742(3)	0.14469	135.72835(26)	0.54014	145.68432(29)	0.60701	5.44572(29)	0.66141(62)
12 CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CD <sub>2</sub> F	22.84591(4)	0.14399	136.79411(26)	0.54051	146.87384(30)	0.61007	6.38309(30)	1.59878(63)
13 СН <sub>3</sub> СНЪСН <sub>2</sub> F	20.79376(2)	0.14443	135.69323(15)	0.53919	145.55664(13)	0.60812	5.46517(15)	0.68086(47)
gauche Isomer								
1 CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> F	34.84447(10)	0.25670	99.36972(31)	0.71360	117.65807(33)	0.90189	8.27806(37)	
2 <sup>13</sup> CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> F	35.14554(13)	0.25828	101.89507(47)	0.71170	120.45677(43)	0.90221	8.29192(47)	0.01387(84)
3 CH <sub>3</sub> <sup>13</sup> CH <sub>2</sub> CH <sub>2</sub> F	35.32732(13)	0.25622	99.98051(42)	0.71518	118.58037(47)	0.90080	8.36374(51)	0.08568(88)
4 CH <sub>3</sub> CH <sub>1</sub> <sup>3</sup> CH <sub>2</sub> F	35.29453(7)	0.25819	99.88314(22)	0.71216	118.43680(25)	0.90184	8.37043(27)	0.09238(64)
5 CD <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> F	38.97538(20)	0.27531	111.58666(64)	0.71809	130.80247(71)	0.90186	0.87979(78)	1.60173(115)
6 CH <sub>2</sub> DCH <sub>2</sub> CH <sub>2</sub> F-1	35.17831(12)	0.26033	106.07367(45)	0.70997	124.49393(43)	0.90062	8.37903(50)	0.10097(87)
7 CH2DCH2CH2F-3	36.53463(9)	0.25170	103.77817(28)	0.71381	120.99256(29)	0.90977	9.66012(33)	1.38206(70)
8 CH <sub>2</sub> DCH <sub>2</sub> CH <sub>2</sub> F-4	37.04884(13)	0.27225	100.60451(36)	0.72370	121.05226(41)	0.90899	8.30055(45)	0.02249(82)
9 CHD <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> F-1,3	36.88873(24)	0.25569	110.39863(104)	0.71018	127.62575(84)	0.90958	9.83081(106)	1.55275(143)
10 CHD <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> F-1,4	37.30479(27)	0.27551	107.26718(96)	0.71757	127.78035(97)	0.90578	8.39581(110)	0.11775(147)
11 CHD <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> F-3,4	38.69030(17)	0.27150	105.01605(48)	0.72212	124.26291(52)	0.90181	9.72172(58)	1.44367(95)
12 CH <sub>3</sub> CD <sub>2</sub> CH <sub>2</sub> F	39.54954(11)	0.25662	103.09868(27)	0.72143	122.35718(30)	0.89756	10.14552(34)	1.86746(71)
13 CH <sub>3</sub> CHDCH <sub>2</sub> F-6	37.18781(12)	0.25740	101.58965(35)	0.71278	118.51877(36)	0.89639	10.12935(41)	1.85129(78)
14 CH <sub>3</sub> CHDCH <sub>2</sub> F-7	36.26020(12)	0.25588	100.86300(34)	0.71869	121.55939(41)	0.89847	8.28191(44)	0.00385(81)
15 CH <sub>3</sub> CH <sub>2</sub> CD <sub>2</sub> F	39.14047(15)	0.26811	103.24498(40)	0.71232	121.98914(41)	0.89865	10.19815(48)	1.92010(85)
16 CH <sub>3</sub> CH <sub>2</sub> CHDF-9	36.94042(7)	0.26459	100.98817(20)	0.71233	121.36080(23)	0.89777	8.28389(25)	0.00584(62)
17 CH <sub>3</sub> CH <sub>2</sub> CHDF-10	37.08652(9)	0.25992	101.62340(27)	0.70950	118.33638(28)	0.89965	10.18677(32)	1.90871(69)
<sup>a</sup> Figures in parenthes	ies indicate the	uncertaint	ies attached to th	e last digit. <sup>b</sup>	$\delta I_{\alpha} = I_{\alpha}(\text{obs}) - I$	a (calc), g =	$a, b, c, I_{a}(calc)$	was calculated
from the coordinate	values listed in	Table 2. <sup>c</sup> l	$\sigma_c = (I_a + I_b - I_c)$	$2.^{d}\Delta P_{c} = P_{c}$	$(isotopic) - P_c$	(normal).		

Moments of inertia (amu A<sup>2</sup>)<sup>a</sup> of propyl fluoride

**TABLE 3** 

15

	Parameter	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> F		CH <sub>3</sub> CH <sub>2</sub> SiH <sub>2</sub> F	
		trans	gauche	trans	gauche
Skeleton	$r(C^{2}-C^{5})(Å)$ $r(C^{5}-X^{8})(Å)$ $r(X^{8}-F)(Å)$ $\alpha(CCX)$ $\alpha(CXF)$ $\delta^{e}$	1.534(1) 1.501(2) 1.401(3) 110°38'(18') 109°58'(25') 180°	1.526(3) 1.506(2) 1.390(5) 112°57'(19') 110°3'(33') 62°36'(27')	1.539(14) 1.852(52) 1.613(95) 111°35′(6°21′) 109°23′(11°31′) 180°	1.535(3) 1.851(5) 1.590(13) 113°51'(33') 109°4'(1°1') 60°14'(45')
C-XH <sub>2</sub> -F	$r(XH^{9})$ (Å) $r(XH^{10})$ (Å) $\alpha(FXH^{9})$ $\alpha(FXH^{10})$ $\alpha(CXH^{9})$ $\alpha(CXH^{10})$ $\alpha(CXH^{10})$	1.095(1) 107°13'(14') 111°35'(8') 109°1'(9')	1.097(4) <sup>b</sup> 1.097(1) 106° 47'(52') 107° 43'(31') 112° 25'(39') 110° 19'(15') 109° 22'(50')	1.471(24) 107°25'(3°58') 111°6'(3°27') 110°13'(3°58')	1.484(6) 1.482(7) 107°11'(1°16') 106°58'(1°12') 112°9'(41') 110°21'(36') 110°52'(53')
C <sup>2</sup> CH <sub>2</sub> X	r(CH <sup>6</sup> ) (Å) r(CH <sup>7</sup> ) (Å) α(XCH <sup>6</sup> ) α(XCH <sup>7</sup> ) α(C <sup>2</sup> CH <sup>6</sup> ) α(C <sup>2</sup> CH <sup>7</sup> ) α(HCH)	1.094(1) 108 <sup>°</sup> 57'(8') 110 <sup>°</sup> 26'(10') 107 <sup>°</sup> 18'(12')	1.099(2) 1.099(6) <sup>b</sup> 107°52'(18') 107°53'(44') 111°9'(24') 110°14'(54') 106°57'(1°11')	1.073(28) 109°59'(5°26') 109°19'(2°36') 106°28'(6°8')	1.087(2) 1.085(2) 107°6'(23') 107°39'(20') 113°12'(24') 112°13'(28') 101°56'(25')
сн,	$r(CH^{1}) (Å)r(CH^{3}) (Å)r(CH^{4}) (Å)a(CCH^{4}) (Å)a(CCH^{3})a(CCH^{4})a(H^{1}CH^{3})a(H^{1}CH^{4})a(H^{3}CH^{4})\gamma^{C}hd$	1.084(2) 1.093(2) 111°21'(25') 110°59'(14') 107°41'(20') 107°57'(27') 111°6'(17') -14'(26')	$\begin{array}{c} 1.086(3) \\ 1.102(4) \\ 1.102(9)^{\rm b} \\ 111^\circ 36' (35') \\ 110^\circ 17' (1^\circ 5') \\ 110^\circ 17' (1^\circ 5') \\ 107^\circ 43' (42') \\ 110^\circ 51' (1^\circ 37') \\ 106^\circ 9' (2^\circ 18') \\ 110^\circ 38' (44',) \\ -58' (55') \end{array}$	$1.083(10)$ $1.074(12)$ $112^{\circ}14'(2^{\circ}42')$ $111^{\circ}30'(1^{\circ}7')$ $106^{\circ}44'(1^{\circ}8')$ $107^{\circ}48'(2^{\circ}37')$ $111^{\circ}44'(1^{\circ}38')$ $-29'(2^{\circ}33')$	$\begin{array}{c} 1.087(2) \\ 1.104(3) \\ 1.104(8)^{\rm b} \\ 112^\circ 4'(35') \\ 110^\circ 1'(35') \\ 112^\circ 35'(1^\circ 56') \\ 106^\circ 45'(34') \\ 111^\circ 33'(1^\circ 41') \\ 103^\circ 18'(3^\circ 33') \\ 111^\circ 33'(1^\circ 1') \\ -30'(1^\circ 13') \end{array}$

rs Structural parameters of propyl fluoride and ethyl fluorosilane<sup>a</sup>

<sup>a</sup>Figures in parentheses indicate uncertainties attached to the last digit. <sup>b</sup>Obtained under one of the assumptions of  $r(CH^5) = r(CH^{10})$ ,  $r(CH^6) = r(CH^7)$ , and  $r(CH^3) = r(CH^4)$ .  $c_{\gamma} = [\alpha(CCH^1) + \alpha(CCH^3) + \alpha(CCH^4)]/3$ ; unperturbed  $\alpha(CCH)$ . <sup>d</sup> $\theta = (2/3)[(\alpha(CCH^3) + \alpha(CCH^4))/2 - \alpha(CCH^1)]$ ; tilt angle of the methyl group. <sup>e</sup>Skeletal dihedral angle around the C<sup>5</sup>-X<sup>8</sup> bond.

# Ethyl fluorosilane

As already pointed out in a previous paper [1], the b-dipole component of the trans isomer is very small so that the b-type transitions could not be measured. Then the A rotational constant could not be determined in sufficient accuracy from the observed a-type transition frequencies since the trans isomer is very close to the symmetric top molecule. In the previous paper [1], the rotational constants were obtained so as to fit the observed a-type transition frequencies with a modified rigid rotor formula which contained the first term  $(d_J)$  of the centrifugal distortion formula for all the measured species. In order to check the results, the calculations were repeated, and identical results were obtained since the  $d_J$  term of the van Eijck type is the same as that of the formula used previously. However, it was found that some of the reported observed frequencies of the transitions having fast Stark effects exhibit relatively large differences from those calculated. Then, we decided to remeasure the frequencies of all the species of both isomers for some of the important transitions. The rotational constants of the *trans* isomer were obtained to fit about fifteen newly observed *a*-type transition frequencies having  $J \leq 6$  and  $k_p \leq 1$ .

For the normal species, the A rotational constant was 17349.951 MHz with a very large uncertainty of 11.653 MHz which is about two thousand times larger than those of the B and C rotational constants.

For the isotopic species, the A rotational constants can be fixed if the  $\Delta P_c$  values (equal to  $P_c$  (isotopic)  $-P_c$  (normal) where  $P_c = (I_a + I_b - I_c)/2$ ) are transferred from those of the analogous molecules and the A rotational constant value of the normal species is regarded as correct. The  $\Delta P_c$  values actually assumed were taken from those of the corresponding species of trans-propyl fluoride and of methyl fluorosilane [10] and are given in Table 5.

The moments of inertia and the coordinate values of the atoms in the molecule were calculated from the rotational constants thus obtained. It was found that the uncertainty of the assumed A rotational constant of the normal species does not affect the calculated coordinate values so much since the coordinate values remain unchanged as the A constant is shifted by  $\pm 100.0$  MHz.

On the other hand, the  $\Delta P_c$  values assumed give large influences on the calculated coordinate values.

For the gauche isomer, the rotational constants were obtained so as to fit about twenty newly observed transition frequencies having  $J \leq 6$  and  $k_p \leq 1$ with a modified rigid rotor formula which contained  $d_J$ ,  $d_{JK}$  and  $\delta_J$  terms of the centrifugal distortion formula.

Details of the observed frequencies, rotational constants, centrifugal distortion constants and the solved coordinate values of the atoms have been deposited at B.L.L.D. (Supplementary Publication No. S.U.P. 26293 (19 pp)).

The structural parameter values calculated from the coordinate values are given in Table 4 and the observed and calculated moments of inertia are listed in Table 5.

For the trans isomer, the r.m.s. value for all the isotopic species (9 species) is 0.1229 amu  $\Lambda^2$ . Since the differences between the observed and calculated  $I_c$  values are negative for all the species used while  $\delta I_a$  and  $\delta I_b$  values are positive, some of the assumed  $\Delta P_c$  values seem to have small differences from the actual values. However, we could not at present, make further corrections for the assumed  $\Delta P_c$  values.

For the gauche isomer, the r.m.s. value for all the species (12 species) is 0.7515 amu  $Å^2$  and the  $I_{ab}$ ,  $I_{ac}$  and  $I_{bc}$  values are 0.1441, -0.1695 and 0.3919 amu  $Å^2$ , respectively. These values are considered to be reasonable when we compare them with the corresponding values for gauche-propyl fluoride.

	$I_a^{ m b}$	$\delta I_a^c$	$I_b$	$\delta I_b^{c}$	Ic	$\delta I_c^c$	$P_c^{\rm d}$	$\Delta P_c^{e}$
trans Isomer CH_JCH_JSH_F <sup>13</sup> CH_JSH_F CH_JCH_SH_F CH_JCH_SH_F CH_JCH_SH_F CH_JCH_SH_F CH_JCH_SH_F CH_JCHDSH_F CH_SHDF CH_SHDF CH_SHDF CH_SHDF	29.12838(1956) 29.13878(2179) 29.57203(2133) 29.55021(2231) 29.43222(2163) 30.35390(2166) 31.56229(2161) 31.56229(2161) 32.28070(2161) 35.47429(2177)	0.12432 0.12519 0.12519 0.12340 0.12346 0.12426 0.12426 0.12426 0.12431 0.11225	175.99023(43) 181.26439(59) 176.93621(37) 176.93621(37) 176.21439(61) 185.97045(55) 182.45589(53) 182.45589(53) 177.53191(50) 177.53191(50) 179.40373(57)	0.00912 0.00918 0.00820 0.00795 0.01963 0.01963 0.00890 0.00844 0.00654	192.93085(52) 198.21535(70) 194.32232(45) 193.37918(118) 193.1992(67) 195.59060(60) 195.03581(60) 196.73581(60)	-0.17048 -0.16961 -0.17048 -0.17048 -0.17048 -0.17048 -0.16979 -0.16893 -0.16893	6.09388(1025) 6.09391(1154) 6.09296(1107) 6.09271(1205) 6.10437(1137) 6.79441(1141) 6.75529(1136) 7.38840(1136) 9.03972(1152)	0.00003( <sup>13</sup> CH <sub>3</sub> CH <sub>3</sub> CH <sub>3</sub> CH <sub>3</sub> CH <sub>3</sub> F) -0.00017(CH <sub>3</sub> <sup>3</sup> SiH <sub>3</sub> F) -0.00117(CH <sub>3</sub> <sup>3</sup> SiH <sub>3</sub> F) 0.01049(s-CH <sub>2</sub> DCH <sub>2</sub> CH <sub>2</sub> F) 0.10053(g-CH <sub>3</sub> DCH <sub>2</sub> CH <sub>3</sub> F) 0.66141(CH <sub>3</sub> CHDCH <sub>2</sub> F) 1.29452(CH <sub>3</sub> SiHDF) 2.94584(CH <sub>3</sub> SiD <sub>2</sub> F)
gauche Isomer CH <sub>3</sub> CH <sub>3</sub> CH <sub>3</sub> CH <sub>3</sub> F <sup>13</sup> CH <sub>3</sub> CH <sub>3</sub> SH <sub>4</sub> F CH <sub>3</sub> OH <sub>3</sub> SH <sub>4</sub> F CH <sub>3</sub> DCH <sub>3</sub> SH <sub>4</sub> F CH <sub>3</sub> DCH <sub>3</sub> SH <sub>4</sub> F CH <sub>3</sub> DCH <sub>3</sub> SH <sub>4</sub> F-3 CH <sub>4</sub> DCH <sub>3</sub> SH <sub>4</sub> F-3 CH <sub>3</sub> DCH <sub>3</sub> SH <sub>4</sub> F-6 CH <sub>3</sub> CHDSH <sub>4</sub> F-6 CH <sub>3</sub> CHDSH <sub>4</sub> F-7 CH <sub>3</sub> CHDSH <sub>4</sub> F-10 CH <sub>3</sub> CH <sub>2</sub> SHDF-9 CH <sub>3</sub> CH <sub>2</sub> SHDF-10 CH <sub>3</sub> CH <sub>2</sub> SHDF-10	$\begin{array}{c} 49.28927(25)\\ 49.28927(25)\\ 49.61097(155)\\ 49.61097(155)\\ 49.59575(15)\\ 51.747473(15)\\ 51.747473(15)\\ 51.74742(27)\\ 51.656825)\\ 51.656825)\\ 51.65687(55)\\ 52.16587(55)\\ 52.16587(55)\\ 51.16587($	0.22043 0.22083 0.22086 0.22188 0.22188 0.221626 0.211626 0.211626 0.20736 0.21187 0.221487 0.22853 0.22853 0.221487	$\begin{array}{c} 139.79794(39)\\ 143.6582(37)\\ 141.15682(37)\\ 141.15682(37)\\ 140.24840(65)\\ 140.24840(65)\\ 145.49295(55)\\ 145.49295(55)\\ 145.12439(77)\\ 142.18709(36)\\ 142.18709(36)\\ 142.20517(60)\\ 142.38023(42)\\ 145.38022(42)\\ 145.38022(42)\\ $	0.77052 0.77037 0.77864 0.76662 0.766622 0.76327 0.76327 0.74459 0.74759 0.74759 0.78811 0.788196 0.782555 0.73265	166.73029(44) 170.86767(40) 168.18884(39) 167.44246(100) 175.88555(37) 170.99023(64) 171.49248(41) 171.49248(41) 171.26879(73) 171.26879(73) 171.2633(45) 172.29728(47)	1.02908 1.02683 1.02683 1.02134 1.03153 1.03017 1.013017 1.01302 1.01706 1.01156 1.01156 1.04392	$\begin{array}{c} 1117846(54)\\ 1122078(49)\\ 1122078(49)\\ 1120846(161)\\ 1120846(161)\\ 1120835(41)\\ 1279907(75)\\ 1279907(75)\\ 127229(88)\\ 1125103(78)\\ 1138114(53)\\ 1139314(53)\\ 11381088(55)\\ 112441(72)\end{array}$	$\begin{array}{c} 0.04232(103)\\ 0.18126(102)\\ 0.18126(102)\\ 0.02999(215)\\ 0.02189(95)\\ 1.62061(128)\\ -1.00735(103)\\ 2.2483(142)\\ 0.07257(131)\\ 0.21468(107)\\ 2.63241(109)\\ 2.94595(126)\end{array}$
aThe figures in was obtained by	parentheses ind the observed a	icate the z-type tra	uncertainty att nsition frequer	ached to acies thou	the last digit. <sup>b</sup> F ugh the uncertai	or the <i>tran</i> nty is fairly	s isomer, the $I_a$ ' r large. The $I_a$ va	value of the normal species lues of the isotopic species

were obtained from the  $I_a$  values of the normal species assuming that the  $\Delta P_c$  values ( $P_c$  (isotopic) –  $P_c$  (normal)) were identical to the related isotopic species of the analogous molecules.  ${}^{c}\delta I_g = I_g$  (obs) –  $I_g$  (calc); g = a, b, c.  ${}^{d}P_c = (I_a + I_b - I_c)/2$ .  ${}^{e}\Delta P_c = P_c$  (isotopic) –  $P_c$  (normal); for the trans isomer, the molecule in the parentheses indicates that those  $\Delta P_c$  values are transferred.

Moments of inertia (amu Å) of ethyl fluorosilane

**TABLE 5** 

18

# Ethylmethyl sulfide

For the *trans* isomer, the rotational constants were obtained to fit the observed frequencies with a modified rigid rotor formula which contained only the  $d_J$  centrifugal distortion term in the previous paper [2]. The calculations were repeated and the reported rotational constants were well reproduced. For the *gauche* isomer, all the five terms of the centrifugal distortion terms,  $d_J$ ,  $d_{JK}$ ,  $d_K$ ,  $d_{EJ}$  and  $d_{EK}$ , were considered for the determination of the rotational constants in the previous paper [3]. The calculations were carried out by use of the formula which contained all five terms ( $d_J$ ,  $d_{JK}$ ,  $d_K$ ,  $\delta_J$  and  $R_6$ ) of the van Eijck type expression for the centrifugal distortion. However, the rotational constants obtained were essentially equal to the old values within experimental uncertainty. Therefore, the moments of inertia,  $r_s$  coordinate values of atoms, and the structural parameter values are almost the same as reported previously.

### DISCUSSION

# Comparison of the r<sub>s</sub> structures of propyl fluoride and ethyl fluorosilane

As shown in Table 4, the  $r_s$  structures of propyl fluoride and ethyl fluorosilane exhibit surprisingly similar features concerning the differences of parameter values between the *trans* and *gauche* isomers, though the experimental uncertainty sometimes exceeds the characteristic differences of the values.

The structural parameter values of the *trans* and *gauche* isomers will be hereafter denoted as  $r_t(C^2C^5)$ ,  $\alpha_g(CCX)$  and so on where X indicates the C<sup>8</sup> carbon atom for propyl fluoride and the Si atom for ethyl fluorosilane, respectively. Furthermore, the average of two parameter values will be denoted as  $\alpha_g^{av}(FXH^9, FXH^{10})$  and so on. The following features can be seen from the table.

(1) Skeleton.  $r_t(C^2C^5) > r_g(C^2C^5)$ ,  $r_t(XF) > r_g(XF)$ ,  $\alpha_t(CCX) < \alpha_g(CCX)$ ,  $\alpha_t(CXF) \doteq \alpha_g(CXF)$ . For propyl fluoride,  $r_t(C^5X) < r_g(C^5X)$ , while  $r_t(C^5X) \doteq r_g(C^5X)$  for ethyl fluorosilane.

(2)  $F - XH_2 - C$  group.  $r_t(XH) < r_g(XH)$ ,  $\alpha_t(HXF) \doteq \alpha_g^{av}(H^9XF, H^{10}XF)$ ,  $\alpha_t(CXH) \doteq \alpha_g^{av}(CXH^9, CXH^{10})$ .

(3)  $C - CH_2 - X$  group.  $r_t(CH) < r_g(CH)$ ,  $\alpha_t(XCH) > \alpha_g^{av}(XCH^6, XCH^7)$ . For propyl fluoride,  $r_t(C^2CH) \doteq r_g^{av}(C^2CH^6, C^2CH^7)$ , while  $r_t(C^2CH) < r_g^{av}(C^2CH^6, C^2CH^7)$  for ethyl fluorosilane.

(4) CH<sub>3</sub> group.  $r(CH^{3,4}) < r_t^{av}(CH^3, CH^4), \alpha_t(CCH^1) \doteq \alpha_g(CCH^1), \alpha_t(H^1CH^{3,4}) < \alpha_g^{av}(H^1CH^3, H^1CH^4).$ 

For propyl fluoride,  $\alpha_t(\text{CCH}^{3,4}) > \alpha_g^{av}(\text{CCH}^3, \text{ CCH}^4)$ , while  $\alpha_t(\text{CCH}^{3,4}) \doteq \alpha_g^{av}(\text{CCH}^3, \text{ CCH}^4)$  for ethyl fluorosilane. The methyl groups of both isomers for both molecules have negligible tilt angle values except for the gauche isomer of propyl fluoride which has a tilt angle value of about 1° toward the H<sup>6</sup> and H<sup>7</sup> hydrogen atoms, though the uncertainty is close to its absolute value.

# Comparison of skeletal structures between analogous molecules

The skeletal structural parameter values of analogous molecules are listed in Table 6. The *trans* and *gauche* isomers of a series of molecules listed exhibit similar features on their CCX angles; that is, the CCX angle value of the *gauche* isomer is markedly larger than that of the *trans* isomer. On the other hand, the CXY angle values remain unchanged within experimental uncertainty except that of ethylmethyl sulfide where the CXY value of the *gauche* isomer is larger by 1°20' than that of the *trans* isomer, in a similar manner as for the CCX angle. When the CXY angle is constant, the features of the CCX angle can be illustrated well as in Fig. 2, where the skeletal internal rotation axis is not coincident with the CX bond but is inclined by  $\theta$  against the CX bond and passes through the carbon atom of the CH<sub>2</sub> group. The unperturbed CCX angle  $\gamma$  is defined as the angle between the skeletal internal rotation axis and the CH<sub>3</sub>-C bond, while the tilt angle  $\theta$  is defined as the angle between the skeletal internal rotation axis and the C-X bond. The skeletal

## TABLE 6

Comparison of skeletal structural parameter values<sup>a</sup>

	r(CH <sub>3</sub> C) (Å)	$r(CH_2X)(A)$	r(XY)(A)	α(CCX)	α(CXY)	δ
CH,CH,	$CH_{2}F(X = CH_{2})$	Y = F)				
trans	1.534	1.501	1.401	110° 38'	109°58′	180°
gauche	1.526	<u>1.506</u>	1.390	<u>112°57′</u>	110° 3'	62° 36'
CH,CH,	$SiH_2F$ (X = $SiH_2$	, Y = F)				
trans	1,539	1.852	1.613	111° 35′	$109^{\circ}23'$	180°
gauche	1.535	1.851	1.590	<u>113°51'</u>	109° 4'	$60^{\circ}14'$
CH,CH,	$SCH_3$ (X = S, Y	= CH <sub>3</sub> )				
trans	1.530	1.803	1.805	109°28'	98° 58′	180°
gauche	$\overline{1.524}$	1.806	1.801	$114^{\circ}42'$	<u>100° 17′</u>	69° 16′
CH,CH,	SH(X = S, Y = H)	H)				
trans	1.529	1.820	1.322	$108^{\circ}34'$	96°	180°
gauche	1.528	1.814	1.336	<u>113° 37′</u>	96° 30′	61°45′
CH,CH,	SeH (X = Se, Y =	= H)				
trans	1.525	1.962	1.440	108° 43'	93° 30'	180°
gauche	1.524	1.957	1.467	<u>113° 31′</u>	93°5′	61° 39′
CH <sub>3</sub> CH <sub>2</sub>	$CH_2Cl (X = CH_2)$	Y = Cl				
trans	(1.534)	(1.501)	1.814	(110° 38')	(109°58′)	180°
gauche	(1.526)	(1.506)	1.798	$114^{\circ}14'$	112° 32'	63° 44′
CH <sub>3</sub> CH <sub>2</sub>	$SiH_2Cl (X = SiH_2)$	$_{2}, Y = Cl$				
trans	(1.539)	(1.852)	2.070	(111° 35')	(109°23')	180°
gauche	(1.535)	(1.851)	2.064	(113°51')	109° 14'	$62^{\circ}14'$

<sup>a</sup>Larger values are underlined; figures in parentheses indicate the value transferred from the corresponding fluoride molecule.



Fig. 2. Relations among  $\alpha_t$ ,  $\alpha_g$ ,  $\gamma$ ,  $\theta$ ,  $\tau$  and  $\delta$ .

dihedral angle of the *gauche* isomer,  $\delta$ , given in Table 4, is defined as the angle around the CX bond. However, this angle should be defined as the angle around the new axis. When the skeletal dihedral angle of the *gauche* isomer around the the new axis is denoted by  $\tau$ , the following relations among  $\gamma$ ,  $\theta$ ,  $\delta$ ,  $\tau$ ,  $\alpha_t$  and  $\alpha_g$  are found.

$$\gamma = \alpha_t + \theta$$
  

$$\tan \theta = (\cos \alpha_t - \cos \alpha_g) / (\sin \alpha_t + \cos \delta \sin \alpha_g)$$
  

$$1 + \cos \tau = (\cos \alpha_t - \cos \alpha_g) / \sin \theta \sin \gamma$$
(9)

For  $\gamma$  and  $\theta$ , the following approximate relations are also valid.

$$\gamma \doteq (1/3)(\alpha_t + 2\alpha_g)$$
  
$$\theta \doteq (2/3)(\alpha_g - \alpha_t)$$
(10)

The relations (10) are those which we use for the tilt of the methyl group.

The  $\gamma$ ,  $\theta$ ,  $\delta$  and  $\tau$  values obtained from the CCX angle values are given in Table 7. The values obtained from the CSC angle values are also given in the table for ethylmethyl sulfide. It is found that the  $\gamma$  values of propyl fluoride and ethyl fluorosilane are very close to the CCX angle values of propane [11] and ethyl silane [12], respectively. As for the  $\theta$  values, the values of propyl fluoride and ethyl fluorosilane are very close to each other, close to the methyl tilt angle value of methyl fluorosilane [10], and smaller than the values of the molecules which have an S or Se atom. The skeletal tilt angle values of sulfide, thiol and selenol are larger by about 1°20' than the methyl tilt angle values of the corresponding molecules [13–15]. This fact suggests

Angle	Compound	Angle	Value	
$\overline{X = C, Si, S}$ $\alpha(CCX)$	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> F	Υ θ δ τ	112°13'(112°10') 1°35'(1°32') 62°36' 62°1'	112°24′(CH <sub>3</sub> CH <sub>2</sub> CH <sub>3</sub> )
	CH <sub>3</sub> CH <sub>2</sub> SiH <sub>2</sub> F	γ θ δ τ	113° 5′(113° 5′) 1° 31′(1° 31′) 60° 14′ 59° 40′	113°11′(CH <sub>3</sub> CH <sub>2</sub> SiH <sub>3</sub> ) 1°45′(CH <sub>3</sub> CH <sub>2</sub> F)
	CH <sub>3</sub> CH <sub>2</sub> SCH <sub>3</sub>	γ ε δ τ	113°18'(112°57') 3°50'(3°29') 69°16' 67°41'	2°30'((CH <sub>3</sub> ) <sub>2</sub> S)
	CH₄CH₂SH	Υ θ δ τ	111° 58'(111° 56') 3° 24'(3° 22') 61° 45' 60° 30'	
	CH <sub>3</sub> CH <sub>2</sub> SeH	γ ε δ τ	111° 57'(111° 55') 3° 14'(3° 12') 61° 39' 60° 28'	$2^{\circ}((CH_3)_2Se)$
α(CSC)	CH <sub>3</sub> CH <sub>2</sub> SCH <sub>3</sub>	γ θ δ τ	99°56'(99°50') 58'(53') 69°16' 69°6'	98°51′((CH <sub>3</sub> ) <sub>2</sub> S)

Skeletal unperturbed angles and tilt angles<sup>a</sup>

<sup>a</sup>Figures in parentheses indicate the values calculated by eqn. (10).

that the skeletal tilt angle arises from two different sources, one from the source which produces the tilted methyl group for the molecules such as dimethyl sulfide and the other from that which produces the skeletal tilt angle of propyl fluoride and the tilted methyl group of methyl fluorosilane. A comparison of the skeletal bond lengths between the *trans* and *gauche* isomers shows interesting features. The first five molecules given in Table 6 can be classified into two groups. For fluorides and sulfide, the bond nearly parallel to the skeletal internal rotation axis is equal or a little larger for the *gauche* isomer than for the *trans* isomer, while the two other bonds for the shand, for thiol and selenol, the CC bonds stay constant between the *trans* and *gauche* isomers, while the other two bonds show the opposite features to the cases of fluorides and sulfide.

In order to check the above features of the skeletal bond and angles, the

skeletal structural parameter values were checked for propyl chloride and ethyl chlorosilane.

For propyl chloride, Sarachman [16] and Yamanouchi et al. [17] reported the results from microwave spectroscopy and gas electron diffraction for the normal species. They found that both the CCX and CXY angles of the *gauche* isomer are much larger than those of the *trans* isomer.

For ethyl chlorosilane, Typke et al. [18] reported the microwave spectra of the normal and three deuterated species.

Since the reported rotational constants are not sufficient to get the  $r_s$  structures for both molecules, the  $r_0$  values of r(XY),  $\alpha(CXY)$ , and  $\delta$  were fixed so as to fit the reported moments of inertia with those calculated, while the other parameter values are transferred from those of propyl fluoride and ethyl fluorosilane.

For the *trans* isomers of propyl chloride and ethyl chlorosilane, the reported moments of inertia are easily reproduced merely by adjusting r(XY) values. The r.m.s. values for all the reported species (two for propyl chloride and five for ethyl chlorosilane) are 0.7843 and 0.1447 amu Å<sup>2</sup>, respectively which are as good as the cases of propyl fluoride and ethyl fluorosilane. For the *gauche* isomer of ethyl chlorosilane, the adjustment of r(XY),  $\alpha(CXY)$  and  $\delta$  values produced a good r.m.s. value (0.4745 amu Å<sup>2</sup>). On the other hand, a very large r.m.s. value was obtained for the *gauche* isomer of propyl chloride when adjustments of r(XY),  $\alpha(CXY)$  and  $\delta$  values had been made. Then, adjustment of the  $\alpha(CCX)$  value was also necessary in order to reduce the r.m.s. value (0.2294 amu Å<sup>2</sup>). The results are given in Table 6.

The  $\delta$  values for the chlorides are found to be a little larger than those for the fluorides. The r(XY) values are similar to those for the fluorides. Concerning the values of  $\alpha(CXY)$ , ethyl chlorosilane shows similar features to those of ethyl fluorosilane, while the *gauche* isomer of propyl chloride has a larger  $\alpha(CXY)$  value by 1° 30' than that of the *trans* isomer, similar to those of ethylmethyl sulfide.

### ACKNOWLEDGEMENTS

The authors wish to express their gratitude to Messrs. Yoshinori Sanemoto and Shigehiro Yoshida for their assistances in the preparation of the samples and spectral measurements.

#### REFERENCES

- 1 M. Hayashi, M. Imachi and M. Oyamada, J. Mol. Struct., 74 (1981) 97.
- 2 M. Hayashi, M. Adachi and J. Nakagawa, J. Mol. Spectrosc., 86 (1981) 129.
- 3 M. Adachi, J. Nakagawa and M. Hayashi, J. Mol. Spectrosc., 91 (1982) 381.
- 4 M. Hayashi, H. Imaishi and K. Kuwada, Bull. Chem. Soc. Jpn., 47 (1974) 2382.
- 5 J. Nakagawa, K. Kuwada and M. Hayashi, Bull. Chem. Soc. Jpn., 49 (1976) 3420.
- 6 J. Nakagawa, H. Okutani and M. Hayashi, J. Mol. Spectrosc., 94 (1982) 410.
- 7 E. Hirota, J. Chem. Phys., 37 (1962) 283.

- 8 B. P. van Eijck, J. Mol. Spectrosc., 53 (1974) 246.
- 9 H. D. Rudolph, J. Mol. Spectrosc., 89 (1981) 460.
- 10 Y. Shiki, M. Oyamada and M. Hayashi, J. Mol. Spectrosc., 92 (1982) 375.
- 11 D. R. Lide, Jr., J. Chem. Phys., 33 (1961) 1514.
- 12 H. D. Petersen, Thesis, University of Notre Dame, 1961.
- 13 L. Pierce and M. Hayashi, J. Chem. Phys., 35 (1961) 479.
- 14 M. Hayashi and N. Nakata, to be published.
- 15 J. Beecher, J. Mol. Spectrosc., 21 (1966) 444.
- 16 T. N. Sarachman, J. Chem. Phys., 39 (1963) 469.
- 17 K. Yamanouchi, M. Sugie, H. Takeo, C. Matsumura and K. Kuchitsu, J. Phys. Chem., 88 (1984) 2315.
- 18 V. Typke, M. Dakkouri and W. Zeil, Z. Naturforsch., Teil A, 29 (1974) 1081.