

Vibrational Assignments and Rotational Isomerism of Dichloroethylmethylsilane and 2,2-Dichlorobutane

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The vibrational spectra of dichloroethylmethylsilane and 2,2-dichlorobutane have been measured. The vibrational assignments of these molecules have been made in relation to the rotational isomerism. The normal vibration calculations based on the modified Urey-Bradley force field have been carried out and have confirmed for both molecules that, in the liquid state, the *trans* and *gauche* isomers coexist, while the *trans* isomer alone persists in the crystalline state.

A number of studies concerning rotational isomerism around a C—C bond as an axis have been reported.¹⁾ Recently, the existence of the rotational isomers around a C—Si bond in the homologous series of alkylsilanes has become apparent.²⁾ We have taken an interest in studying the rotational isomerism in the homologous series of alkylsilanes. In this paper, we will deal with the vibrational assignments and the rotational isomerism of dichloroethylmethylsilane and its analogues, *viz.*, 2,2-dichlorobutane.

Experimental

Dichloroethylmethylsilane was prepared from methyltrichlorosilane by adding C_2H_5MgBr .³⁾ 2,2-Dichlorobutane was prepared by the reaction of ethyl methyl ketone with PCl_5 .⁴⁾

The infrared spectra in the 250—4000 cm^{-1} region were recorded on a Perkin-Elmer instrument (Model 621). For the measurements in the crystalline state in this region, the vapor was condensed on a CsI window cooled with liquid nitrogen; the sample was then annealed near the melting point. For the spectra of dichloroethylmethylsilane in the 30—400 cm^{-1} region, a Hitachi Fis-3 far-infrared spectrometer equipped with a cell of polyethylene windows was used. The Raman spectra of dichloroethylmethylsilane in the liquid state were recorded on a JEOL Raman spectrometer (Model JRS-02AS), using an argon-ion laser (488.0 nm) for excitation.

Rotational Isomerism

Figure 1 shows the infrared and Raman spectra of $C_2H_5SiCl_2CH_3$ in the region below 900 cm^{-1} . The $SiCl_2$ stretching vibrations can be expected in the 400—600 cm^{-1} region from a comparison of the spectra with those of $(CH_3)_2SiCl_2$.⁵⁾ In the infrared spectra, the very-strong pair band at 546 and 530 cm^{-1} and the strong pair band at 471 and 467 cm^{-1} are observed in the liquid state. In the supercooled liquid state before annealing, the absorption intensities of both the higher-frequency bands of the pairs are weaker than the lower-frequency bands, while the reverse is true in the liquid state. In the crystalline state, both the lower-frequency bands of the two pairs persist, while the disappeared bands again appear with a rise in the temperature. These results indicate that rotational isomers exist in the liquid state, while one isomer persists in the crystalline state. On the other hand, in the Raman spectra, the very-strong pair counterpart at

460 and 470 cm^{-1} and the very-weak pair counterpart at 531 and 540 cm^{-1} , corresponding to the pair bands around 470 and 540 cm^{-1} respectively in the infrared spectra, are observed in the liquid state; they are, therefore, assigned to the $SiCl_2$ symmetric and antisymmetric stretching vibrations respectively.

On the other hand, Fig. 2 shows the infrared

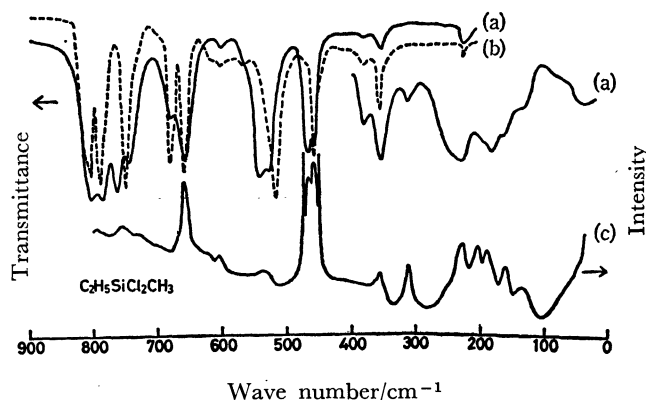


Fig. 1. The vibrational spectra of dichloroethylmethylsilane.

(a): the infrared spectra in the liquid state, (b): the infrared spectra in the crystalline state, (c): the Raman spectra in the liquid state.

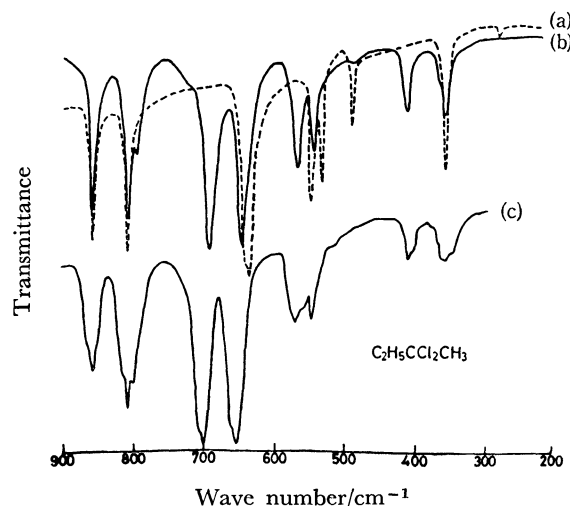


Fig. 2. The infrared spectra of 2,2-dichlorobutane.

(a): in the crystalline state, (b): in the liquid state, (c): in the gaseous state at room temperature.

spectra of 2,2-dichlorobutane in the 250–900 cm^{-1} region. For alkyl chlorides, useful information about the rotational isomerism has been obtained from the C–Cl stretching and skeletal deformation vibrations.¹⁾ In this molecule, the very-strong pair band at 692 and 645 cm^{-1} and the strong pair band at 567 and 544 cm^{-1} in the liquid state, clearly separated from each other, are observed; they are easily assigned to the CCl_2 antisymmetric and symmetric stretching vibrations respectively by reference to the spectra of 2,2-dichloropropane,⁶⁾ while both the higher-frequency bands of the pairs disappear in the crystalline state. In Fig. 2, the split pattern of the band at 544 cm^{-1} in the crystalline state may be due to the influence of the crystalline field because, in the supercooled liquid state before annealing, this pattern is not observed. The tendency of the CCl_2 stretching vibrations is the same as that of the $SiCl_2$ stretching vibrations. Therefore, it may be expected that, for both molecules, only one isomer with the same molecular form persists in the crystalline state, while two isomers coexist in the liquid state.

The results of the normal vibration calculations, which will be given in Tables 4 and 5, indicate that the antisymmetric and symmetric YCl_2 stretching vibrations ($Y=C, Si$) for the *gauche* isomer are higher in frequency than those for the *trans* isomer and that, among the skeletal deformation vibrations, the highest-frequency vibration for the *trans* isomer is higher in frequency than that for the *gauche* isomer. The conclusion regarding the molecular form obtained from the skeletal deformation vibration is consistent with that obtained from the YCl_2 stretching vibrations.

Energy Difference between Isomers. For 2,2-dichlorobutane, the relative intensities of the bands at 692 and 645 cm^{-1} assigned to the CCl_2 antisymmetric stretching vibration for the *gauche* and *trans* isomers respectively are measured in the gaseous state at ten different temperatures; in the crystalline state the former disappears, while the latter persists. Figure 3 shows some typical examples of the infrared bands at 301, 320, 343, 368, and 399 K. From the observed optical densities, the energy difference between the isomers

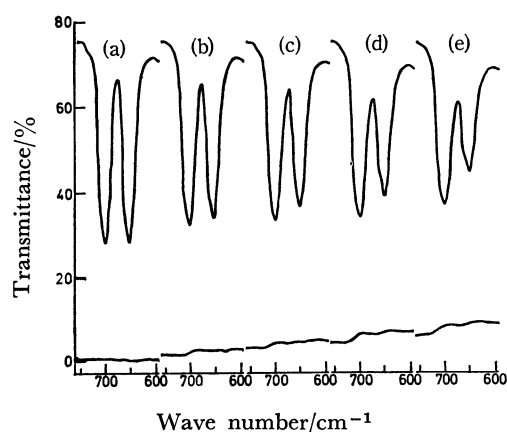


Fig. 3. The relative intensities of the infrared bands at 692 and 645 cm^{-1} in the gaseous state.

Upper: absorption spectra, Lower: base line; (a): at 301 K, (b): at 320 K, (c): at 343 K, (d): at 368 K, (e): at 399 K.

is found to be *ca.* 0.5 kcal/mol, where the *trans* isomer is more stable than the *gauche* isomer. This value is in good agreement with the value estimated by means of the interactions of the atoms in the 1,3 positions lying on parallel bonds which has been presented by Štokr *et al.*⁸⁾ However, for dichloroethylmethylsilane, measurements of the relative intensities of the bands cannot

TABLE 1. VIBRATIONAL FREQUENCIES OF DICHLOROETHYLMETHYLSILANE^{a)} (cm^{-1})

Infrared			Raman		Assignment
Liquid Int.		Crystal Int.	Liquid Int.		
2970	s	2970 s	2975 s		C–H str.
2944	m	2944 m	2943 s		
2917	m	2917 w	2911 vvs		
2885	m	2888 s	2884 vs		
1468 sh	m	1466 m			CCH ₃ asym. def.
1461	m	1455 m	1462 w		
1410	m	1408 m	1406 w		SiCH ₃ asym. def.
1401 sh	m	1399 w			CH ₂ sci.
1384	w	1376 w	1381 vw		CCH ₃ sym. def.
		1366 vw			
1262	vs	1264 s	1261 vw		SiCH ₃ sym. def.
1242	m	1246 m	1241 w		CH ₂ wag.
1232	w	1232 w	1230 vw		CH ₂ twist.
1087 b	w				
1021	m	1025 m	1019 w		C–C str.
1011	s	1015 vw	1011 mw		
974 sh	w	974 vw	973 w		CCH ₃ rock.
965	m	959 m			
806	vs	807 vs	807 vw		SiCH ₃ rock.
788	vs	792 vs			
767	vs	—	766 w		C–Si antisym. str.
748	s	754 vs	746 w		
		705 vw			
685	m	684 s			CH ₂ rock.
662	s	663 vs	662 m		C–Si sym. str.
606	w	609 w	604 w		
		574 w			
		565 w	557 w		
543	vs	—	540 w		SiCl ₂ antisym. str.
531	vs	518 vs	531 w		
		477 w			
470	s	—	470 vvs		SiCl ₂ sym. str.
461	s	459 s	460 vvs		
427	vw		426 vw		
383	w	384 w	383 w		
356	m	356 m	357 mw		
315	vw	—	314 m		
231	m	228 w	231 s		
			199 ms		Skeletal def. or torsion
184	m		183 s		
167 sh	w		164 ms		
138	w		134 m		
			79 mw		

a) Int.=intensity; s, m, w=strong, medium, weak; v=very; sh=shoulder; and b=broad.

TABLE 2. VIBRATIONAL FREQUENCIES OF 2,2-DICHLOROBUTANE^{a)} (cm⁻¹)

Infrared			Raman ^{b)} Liquid Int.	Assignment
Gas Int.	Liquid Int.	Crystal Int.		
(2996 2990 vs 2987	2980 vs	3001 w 2973 s	2986 4b	C-H str.
(2951 2941 vs	2944 s	(2936 m 2921	2936 6b	
2930	2930 sh ms			
2897 sh w	2892 ms 2866 vw	2875 m		
2850 sh w	2848 vw			
(1465 1460 s	1463 s 1454 s	(1465 s 1453 s 1447 s 1443 w	1441 4b	CH ₃ asym. def.
1446	1443 s			
(1438 1432 m	1427 mw	(1436 s 1432		CH ₂ sci.
(1394 sh 1389 s		(1379 s 1376 s 1348 w 1343 m	1380 1 1329 0	CH ₃ sym. def.
1382 vs 1343 w 1335 w	1382 s 1342 w 1332 w			
(1287 1280 m	(1283 sh m 1279	(1284 s 1277	1272 1 1224 0	CH ₂ wag. CH ₂ twist.
1275				
1172 m 1148 b s	1185 w 1170 m 1146 s	1174 s — 1136 m	1167 1	C-C str. or CH ₃ rock.
(1128 vs 1123	1120 s	(1122 s 1111	1113 1	
(1102 1097 vs 1092	1091 s	— 1087 vw 1075 vw	1088 1	
1042	(1042 sh ms 1037	(1034 s 1033	1020 1/2	
1037 s 1030 1007 m 998 m 991	1008 w 999 w	998 s		
982 m (859 s 854	982 m 859 s	— 856 s	977 1 853 2	CH ₂ rock.
(815 809 s 803	808 s 796 m	808 s —	793 0	
(708 701 vs 696	692 vs	—	688 3	
(662 656 vs	645 vs	635 vs	642 3	CCl ₂ antisym. str.

Table 2. Continued

Infrared			Raman ^{b)}		Assignment
Gas Int.	Liquid Int.	Crystal Int.	Liquid Int.		
(572 560 548	m m	567 m 544 m	— 545 s 529 s 488 m	566 4 544 4 486 0 410 2	CCl ₂ sym. str.
(418 413 406	m	413 m	—		
(375 368 365	m	367 sh m	—		
(357 353	m	358 m	356 s 281 vw	362 4 276 2 252 2 202 2	
					Skeletal def. or torsion

a) See a) of Table 1. b) See Ref. 18.

be made because of the overlapping of the bands assigned to the $SiCl_2$ stretching vibrations in the gaseous state.

Vibrational Assignments

The *trans* form of dichloroethylmethylsilane and 2,2-dichlorobutane may have C_s symmetry. The 36 normal modes are reduced by group theory to 21 modes of the A' species and 15 of A'' . The *gauche* form belongs to the trivial point group C_1 . All of the 36 modes are of the same symmetry species. All of the fundamental vibrations of the *trans* and *gauche* forms are infrared and Raman-active. The observed frequencies are given in Tables 1 and 2, together with the brief vibrational assignments.

Dichloroethylmethylsilane. It is expected that the vibrations of the $SiCH_3$ group are considerably lower in frequency than the corresponding vibrations of the CCH_3 group because of the difference in the electronegativity of the adjacent atom. Actually, these vibrations of the CCH_3 and $SiCH_3$ groups are observed at different frequencies clearly separated from each other. The infrared spectra of dichloroethylmethylsilane in the 800–1500 cm^{-1} region are not so different in the liquid and crystalline states, and they are close to the superposition of the spectra of ethyltrichlorosilane⁹⁾ and methyltrichlorosilane.¹⁰⁾ The infrared spectra in the 400–800 cm^{-1} region are also similar to those of dimethyldichlorosilane.⁵⁾ Therefore, the vibrational assignments in the 400–1500 cm^{-1} region can easily be made by a comparison of the spectra with those of analogues. The bands in the region below 400 cm^{-1} may be assigned to the skeletal deformation or torsional vibrations. However, the vibrational assignments in this region cannot be made easily, for a large mode mixing among the several skeletal deformation vibrations must be expected; they are tentatively assigned in Table 4 on the basis of the results of the normal vibration calculations.

2,2-Dichlorobutane. In the infrared spectra in

the 300–1500 cm^{-1} region, as too many bands for a unique molecular form are observed in the liquid state and as several bands vanish in the crystalline state, it may be concluded that rotational isomers coexist in the liquid state, while only one isomer persists in the crystalline state. The infrared spectra show that most of the vibrations of the two CH_3 groups may be coincident with each other, because the presence of one CH_3 group is sufficient to account for the number of observed bands. Therefore, the infrared spectra in the 1200–1500 cm^{-1} region can easily be assigned on the basis of a comparison of the spectra with those of analogues, such as CH_3CCl_3 ¹¹⁾ and CH_3CH_2X .¹²⁾ The bands in the 800–1200 cm^{-1} region may be assigned to the C–C stretching or CH_3 rocking vibrations, but three C–C stretching and four CH_3 rocking vibrations are expected for a unique molecular form and may mix with each other in the same symmetry species. Therefore, the vibrational assignments in this region are made from the results of the normal vibration calculations. On the other hand, the strong infrared bands at 796 and 808 cm^{-1} and the weak Raman counterpart at 793 cm^{-1} are assigned to the CH_2 rocking vibrations. The very-strong pair band around 670 cm^{-1} and the strong pair band around 550 cm^{-1} are easily assigned to the CCl_2 stretching vibrations, as has already been mentioned. The infrared bands in the region below 500 cm^{-1} may be assigned to the skeletal deformation or torsional vibrations. These bands are assigned on the basis of the results of the normal vibration calculations, because large mixings of the modes are expected.

Normal Vibration Calculation

The normal vibrations were calculated on the basis of the modified Urey-Bradley force field in order to determine the molecular forms and the vibrational assignments. The force constants were transferred from those of $CH_3CH_2SiH_3$ ¹³⁾ and $(CH_3)_2SiCl_2$ ⁵⁾ for $C_2H_5SiCl_2CH_3$ and from those of $CH_3CHClCHClCH_3$ ¹⁴⁾

TABLE 3. FORCE CONSTANTS FOR DICHLOROETHYLMETHYLSILANE AND 2,2-DICHLOROBUTANE^{a)}

$C_2H_5SiCl_2CH_3$			
$K(C-H)$	4.297	$Y(C-C)$	0.109
$K(C-C)$	2.400	$Y(C-Si)$	0.052
$K(C-Si)$	1.991	$p(C-H)$	-0.070
$K(Si-Cl)$	2.590 (2.226)	$p(Si-Cl)$	(0.174)
$H(C-C-H), CH_3$	0.164	$F(C \cdot C \cdot H), CH_3$	0.470
$H(H-C-H), CH_3$	0.370	$F(H \cdot C \cdot H), CH_3$	0.200
$H(C-C-Si)$	0.087	$F(C \cdot C \cdot Si)$	0.540
$H(Si-C-H)$	0.123	$F(Si \cdot C \cdot H)$	0.271
$H(C-C-H), CH_2$	0.278	$F(C \cdot C \cdot H), CH_2$	0.540
$H(H-C-H), CH_2$	0.331	$F(H \cdot C \cdot H), CH_2$	0.200
$H(C-Si-C)$	0.110	$F(C \cdot Si \cdot C)$	0.040
$H(C-Si-Cl)$	0.085	$F(C \cdot Si \cdot Cl)$	0.162
$H(Cl-Si-Cl)$	0.059	$F(Cl \cdot Si \cdot Cl)$	0.290
$\kappa(CCH_3)$	0.008	$\kappa(SiCl_2)$	0.130
$\kappa(CH_2)$	-0.040	$\kappa(SiCH_3)$	-0.050
$C_2H_5CCl_2CH_3$			
$K(C-H)$	4.350	$Y(C-C)$	0.109
$K(C-C)$	2.750	$p(C-H)$	-0.086
$K(C-Cl)$	1.697 (1.353)	$p(C-Cl)$	(-0.090)
$H(C-C-H), CH_3$	0.186	$F(C \cdot C \cdot H), CH_3$	0.470
$H(H-C-H), CH_3$	0.370	$F(H \cdot C \cdot H), CH_3$	0.200
$H(C-C-C)$	0.275	$F(C \cdot C \cdot C)$	0.335
$H(C-C-H), CH_2$	0.186	$F(C \cdot C \cdot H), CH_2$	0.470
$H(H-C-H), CH_2$	0.343	$F(H \cdot C \cdot H), CH_2$	0.200
$H(C-C-Cl)$	0.087	$F(C \cdot C \cdot Cl)$	0.747
$H(Cl-C-Cl)$	0.062	$F(Cl \cdot C \cdot Cl)$	0.697
$\kappa(CH_2)$	0.100	$\kappa(CH_3)$	0.008

a) All the force constants are transferred from ethylsilane¹³⁾ and dimethyldichlorosilane⁵⁾ for dichloroethylmethylsilane and from 2,3-dichlorobutane¹⁴⁾ and dichloromethane¹⁵⁾ for 2,2-dichlorobutane. The adjusted force constants are given in brackets. The units of the force constants are in mdyne/Å for stretching, K ; bending, H ; repulsion, F ; and bond-interaction, p ; and in mdyne·Å for intramolecular tension, k ; and internal rotation, Y .

and CH_2Cl_2 ¹⁵⁾ for $C_2H_5CCl_2CH_3$. The following assumptions were made for the force field: 1) the bond-interaction constant, $p(C-H)$, was added in order to reproduce the observed C-H stretching frequencies, 2) the torsional force constant, $Y(C-C)$, was assumed to be the value (3.49 kcal/mol) obtained from the reported far-infrared band for the CH_3 torsion of ethyl chloride¹⁶⁾ and the $Y(C-Si)$ constant was assumed to be the value (1.65 kcal/mol) of dimethylsilane determined by microwave study,¹⁷⁾ and 3) for $C_2H_5SiCl_2CH_3$, the force constants, $H(H-C-H)$ and $F(H \cdot C \cdot H)$, were assumed to be the same values for the CCH_3 and $SiCH_3$ groups, while for $C_2H_5CCl_2CH_3$, the force constants, $H(H-C-H)$, $H(C-C-H)$, $F(H \cdot C \cdot H)$ and $F(C \cdot C \cdot H)$, were assumed to be the same values for both the CH_3 groups.

The force constants used in the calculation are given in Table 3. The vibrational frequencies in the region below 1200 cm^{-1} depend more conspicuously upon the azimuthal angle of internal rotation. Therefore, the observed and calculated frequencies in this region are given in Tables 4 and 5, together with the predominant symmetry coordinates in the potential energy distributions. Set I of the calculation in Tables 4 and 5 shows the calculations using all the transferred

force constants given in Table 3. A fair agreement is obtained between the observed and calculated frequencies, except for a few vibrations. Especially, the calculated frequencies of the YCl_2 stretching ($Y=C, Si$) and the highest-frequency skeletal deformation vibrations indicate that, for both dichloroethylmethylsilane and 2,2-dichlorobutane, the bands persisting in the crystalline state are attributable to the *trans* form, while the bands disappearing in the crystalline state are attributable to the *gauche* form. However, as the calculated YCl_2 stretching frequencies indicate that the values of both the force constants, $K(C-Cl)$ and $K(Si-Cl)$, have to be smaller than the transferred values, only these constants, $K(C-Cl)$ and $K(Si-Cl)$, are adjusted in order to reproduce the observed frequencies. We still cannot reproduce the separations between the YCl_2 antisymmetric and symmetric stretching frequencies satisfactorily. Therefore, the bond-interaction constants, $p(C-Cl)$ and $p(Si-Cl)$, are introduced.

The results of the calculations obtained in this modification are given in Set II of the calculation in Tables 4 and 5. The values of the adjusted force constants are $K(C-Cl)=1.353$, $p(C-Cl)=-0.090$, $K(Si-Cl)=2.226$, and $p(Si-Cl)=0.174$ mdyne/Å. It is inter-

TABLE 4. OBSERVED AND CALCULATED FREQUENCIES OF DICHLOROETHYLMETHYLSILANE (cm^{-1})^{a)}

<i>Trans</i> form				<i>Gauche</i> form				PED
Obsd	Calcd		Obsd	Calcd				
	Set I	Set II		Set I	Set II			
A'	1021	1020	1020	A	1011*	1022	1022	$\nu(\text{C-C})$
	974	968	968		974	968	968	$r(\text{CCH}_3)$
	806	798	797		806	798	797	$r(\text{SiCH}_3)$
					767*	749	748	$\nu_a(\text{C-Si}), r(\text{CH}_2)$
	748	729	729					$\nu_a(\text{C-Si})$
	662	682	679		662	667	663	$\nu_s(\text{C-Si})$
	461	471	460		470*	481	469	$\nu_s(\text{SiCl}_2)$
	356	342	342					$\delta(\text{CCSi}), w(\text{SiCl}_2)$
					315*	319	316	$\delta(\text{CCSi})$
	231	220	220		231	234	234	$\delta(\text{CCSi}), w(\text{SiCl}_2)$
					231	223	223	$w(\text{SiCl}_2), r(\text{SiCl}_2)$
	184	184	184					$s(\text{SiCl}_2), w(\text{SiCl}_2)$
					167	176	176	$s(\text{SiCl}_2), \tau(\text{SiCH}_3)$
	138	134	134					$w(\text{SiCl}_2), s(\text{SiCl}_2), \delta(\text{CSiC})$
A''	965	967	967		965	967	967	$r(\text{CCH}_3)$
	788	796	793		788	795	792	$r(\text{SiCH}_3)$
	685	727	725					$r(\text{CH}_2)$
					685	708	707	$r(\text{CH}_2), \nu_a(\text{C-Si})$
	531	585	531		543*	602	549	$\nu_a(\text{SiCl}_2)$
	—	241	241		—	240	240	$\tau(\text{CCH}_3)$
	231	233	232					$r(\text{SiCl}_2)$
					199	196	196	$r(\text{SiCl}_2), t(\text{SiCl}_2)$
	184	188	188					$t(\text{SiCl}_2)$
					—	154	154	$\tau(\text{SiCH}_3), \delta(\text{CSiC}), s(\text{SiCl}_2)$
	—	152	152					$\tau(\text{SiCH}_3), t(\text{SiCl}_2)$
					138	134	134	$t(\text{SiCl}_2)$
	—	56	56		79	58	58	$\tau(\text{skel})$

a) The observed infrared frequencies in the liquid state are listed, where asterisks indicate the bands disappearing in the crystalline state. The vibrational frequencies below 1200 cm^{-1} are included. Potential energy distributions are shown for the internal symmetry coordinates, where only contributions greater than 20% are included. ν , δ , s , w , t , r , and τ denote the stretching, deformation, scissoring, wagging, twisting, rocking, and torsional modes and a and s denote the antisymmetric and symmetric modes, respectively.

esting to note that the value of $p(C-Cl)$ is negative, while that of $p(Si-Cl)$ is positive. It is also noticeable that the frequency differences of the YCl_2 stretching vibrations between the antisymmetric and symmetric modes and between the *trans* and *gauche* forms for $C_2H_5SiCl_2CH_3$ are smaller than those for $C_2H_5CCl_2CH_3$. This may be because, for the nonlinear YX_2 -type molecule, the off-diagonal element of the **G**-matrix between the stretching modes is $\cos \alpha \mu_Y$ (μ_Y is the reciprocal of the mass of the atom, Y).⁷⁾ Therefore, the separation frequency between the antisymmetric and symmetric modes of the YCl_2 stretching may be mainly affected by the mass of the atom, Y, though the quite reverse influence of the corresponding off-diagonal element of the **F**-matrix containing only the repulsive force constant, $F(Cl \cdot Y \cdot Cl)$, in the simple Urey-Bradley force field ($F' = -0.1F$) can be expected, and though the couplings of the YCl_2 stretching modes with the other modes are not taken into account. In order to predict well the observed YCl_2 stretching frequencies, the bond-

interaction constant, $p(Y-Cl)$, is necessary.

On the other hand, the frequency separation of the YCl_2 stretching modes between the different molecular forms may be mainly influenced by the vibrations of the adjacent groups, which, in combination with the YCl_2 stretching modes, give the off-diagonal **G**-matrix elements containing the azimuthal angle, such as the $Y-C-C$ bending and CH_2 rocking modes for $C_2H_5YCl_2CH_3$ ($Y=C, Si$). The larger couplings are expected from the perturbation theory⁷⁾ when the vibrational frequencies come close to one another. The separations of the YCl_2 stretching modes with both the CH_2 rocking and $Y-C-C$ bending modes for $C_2H_5CCl_2CH_3$ are smaller than those of $C_2H_5SiCl_2CH_3$. Therefore, it can be expected that the separations of the YCl_2 stretching vibrations between the different molecular forms for $C_2H_5CCl_2CH_3$ are larger than those for $C_2H_5SiCl_2CH_3$. This is supported by the results of the potential energy distributions of the modes, given in Tables 4 and 5.

TABLE 5. OBSERVED AND CALCULATED FREQUENCIES OF 2,2-DICHLOROBUTANE (cm⁻¹)^{a)}

<i>Trans</i> form				<i>Gauche</i> form				PED
Obsd	Calcd		Obsd	Calcd				
	Set I	Set II		Set I	Set II			
A'	1170	1156	1153	A	1146*	1154	1150	$\nu(\text{C-C})$
	1120	1112	1108		1091*	1103	1100	$\nu(\text{C-C}), t(\text{CH}_2)$
	1037	1048	1047		1042*	1074	1072	$\nu(\text{C-C})$
	999	989	989		982*	985	985	$\nu(\text{C-C}), r(\text{CH}_3), r(\text{CH}_2)$
	859	876	874		859	873	871	$\nu(\text{C-C})$
	544	576	547		567*	597	568	$r(\text{CH}_3)$
	490	481	479					$r(\text{CH}_3), \nu(\text{C-C})$
								$\nu_s(\text{CCl}_2), \delta(\text{CCC})$
								$\nu_s(\text{CCl}_2)$
								$w(\text{CCl}_2), \delta(\text{CCC})$
					413*	416	409	$w(\text{CCl}_2)$
					367*	377	374	$\delta(\text{CCC}), w(\text{CCl}_2)$
	358	347	345					$\delta(\text{CCC})$
	276	265	265		252	257	257	$s(\text{CCl}_2)$
	202	190	190		202	190	190	$\delta(\text{CCC}), t(\text{CCl}_2), r(\text{CCl}_2)$
A''	1037	1076	1075					$r(\text{CH}_3), r(\text{CH}_2)$
					1008*	1026	1021	$r(\text{CH}_3), \nu(\text{C-C})$
	999	997	996		982*	996	995	$r(\text{CH}_3)$
	808	860	859					$r(\text{CH}_2), r(\text{CH}_3)$
					796*	839	837	$r(\text{CH}_2), r(\text{CH}_3), \nu(\text{C-C})$
					692*	719	691	$\nu_a(\text{CCl}_2), r(\text{CCl}_2), \delta(\text{CCC})$
	645	665	632					$\nu_a(\text{CCl}_2), r(\text{CCl}_2)$
	358	366	364					$r(\text{CCl}_2)$
					358	359	357	$r(\text{CCl}_2), w(\text{CCl}_2)$
	276	302	301		276	302	302	$t(\text{CCl}_2)$
	—	240	240		—	240	240	$\tau(\text{CH}_3)$
	—	222	222		—	228	228	$\tau(\text{CH}_3)$
	—	81	81		—	86	87	$\tau(\text{skel})$

a) See a) of Table 4.

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