

The Vibrational Spectra and Rotational Isomerism of 3-Butenylsilane

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(Received September 9, 1978)

The infrared and Raman spectra of 3-butenylsilane, $\text{CH}_2=\text{CHCH}_2\text{CH}_2\text{SiH}_3$ (and $-\text{SiD}_3$), were measured for the gaseous, liquid, and solid states. The fundamental vibrations were assigned, and the normal vibrations were calculated in relation to the rotational isomerism. The calculations indicated that the *cis-trans* (CT), *skew-trans* (ST), and *skew-gauche* (SG and SG') forms coexist in the gaseous and liquid states, while the CT form only persists in the solid state. From the temperature variation in the Raman intensities, the stability of the molecular conformations was found to be in this order: $\text{CT} \geq \text{ST} > \text{SG}' > \text{SG}$ in the liquid state, indicating that an appreciable interaction between the silicon atom and the C=C bond, such as in the case of allylsilane, is not present for 3-butenylsilane.

The properties of the UV and IR spectra of unsaturated organosilanes have long been investigated and have been commonly cited as evidence of the interaction between vacant 3d-orbitals of the silicon atom and the C=C π electron system, *i.e.*, ($p \rightarrow d$)- π -bonding and long ($p \rightarrow d$) π -bonding.¹⁾ Recently, however, the bathochromic effect of the UV spectra and the abnormal high reactivity to the C=C bond of β -unsaturated organosilanes have been interpreted in terms of the σ - π hyperconjugation between the C=C π and the Si-C σ bonds.²⁾ The magnitude of this hyperconjugation varies with the dihedral angle about the axis between the carbon atoms in the α - and β -positions, and it is maximal at 90° ,³⁾ indicating that the *skew* conformation is preferable to the *cis* conformation. Actually, in a previous paper⁴⁾ the analysis of the vibrational spectra has confirmed that, for allylsilane, only the form near the *skew* form predominantly exists in the gaseous, liquid, and solid states, although, for methylvinylsilane, the *cis* and *skew* forms coexist in the gaseous and liquid states. The same conclusion as to the molecular conformation of allylsilane has also been drawn from the electron-diffraction study⁵⁾ and the microwave spectral analysis.⁶⁾

In the present paper, we will, then, deal with the molecular vibrations and rotational isomerism of 3-butenylsilane in order to obtain information on the interaction between the C=C bond and the silicon atom of the γ -position.

Experimental

The samples of 3-butenylsilane, $\text{CH}_2=\text{CHCH}_2\text{CH}_2\text{SiH}_3$, and its deuterated species, $\text{CH}_2=\text{CHCH}_2\text{CH}_2\text{SiD}_3$, were prepared as follows. Allyl bromide was converted to 3-buten-1-ol using magnesium and paraform, and the 3-buten-1-ol was then converted to 3-bromo-1-butene using PBr_3 , by the method of Linstead *et al.*⁷⁾ A Grignard reagent prepared from the 3-bromo-1-butene was added to silicon tetrachloride in dry ether to yield 3-butenyltrichlorosilane. The resulting 3-butenyltrichlorosilane was reduced to 3-butenylsilane with LiAlH_4 or LiAlD_4 in dry dibutyl ether. The purities of the 3-butenylsilane- d_0 and $-d_3$ were checked by NMR analysis.⁸⁾

The infrared spectra in the $250\text{--}4000\text{ cm}^{-1}$ region and the Raman spectra in the $10\text{--}4000\text{ cm}^{-1}$ region were recorded on a Perkin-Elmer instrument (Model 621) and a JEOL Raman spectrometer (Model JRS-400D) with an argon-ion laser respectively. The infrared and Raman spectra were

measured for the gaseous, liquid, and solid states and for the liquid and solid states respectively, using the technique described in a previous paper.⁴⁾

Results

Normal Coordinate Treatment. A molecule of 3-butenylsilane has two C-C axes and five possible isomers: *cis-trans* (CT), *cis-gauche* (CG), *skew-trans* (ST), *skew-gauche* (SG: stretched), and *skew-gauche'* (SG': bent). In order to confirm the molecular forms and the assignments of the observed spectra to rotational isomers, the normal vibrations were calculated using the modified Urey-Bradley force field. The structural parameters used were transferred from those of 1-butene⁹⁾ and ethylsilane¹⁰⁾ determined by microwave study. All the valence angles except for the $\text{CH}_2=\text{CH}$ group were assumed to be tetrahedral, and the dihedral angles were assumed to be 0° for the C form and 120° for the S form about the $(\text{CH}_2=)\text{CH}-\text{CH}_2(\text{CH}_2)$ axis, and 60° for the G form and 180° for the T form about the $(=\text{CH})\text{CH}_2-\text{CH}_2-\text{SiH}_3$ axis. The force constants used in the present calculation were transferred from those of propylsilane,¹¹⁾ allylsilane,⁴⁾ and olefins,¹²⁾ and the torsional force constants¹³⁾ of $Y(\text{C}-\text{C}=\text{C})$ and $Y(\text{C}-\text{Si})$ were assumed from the barrier heights of 1.7 kcal/mol for 1-butene⁹⁾ and 2.04 kcal/mol for ethylsilane¹⁰⁾ respectively. Tables 1 and 2 give the observed and calculated frequencies of 3-butenylsilane- d_0 (BS- d_0) and 3-butenylsilane- d_3 (BS- d_3), together with the assignments based on the predominant potential energy distributions.

Rotational Isomerism. The molecule of 3-butenylsilane has 15 atoms and has the molecular symmetry of C_s for the CT form and that of C_1 for the CG, ST, SG, and SG' forms. In the C_s symmetry, the 39 normal vibrations are reduced to 24 of the A' species and 15 of the A'' , while in the C_1 symmetry all 39 are of A . All the normal vibrations are infrared and Raman active.

Figures 1 and 2 show that several Raman lines in the liquid state disappear in the solid state, indicating the existence of the rotational isomers in the liquid state. On the other hand, almost all the frequencies observed in the solid state are assigned to the fundamental vibrations for one isomer, as Tables 1 and 2 show.

For such *n*-alkylsilanes as propylsilane and butyl-

TABLE 1. OBSERVED AND CALCULATED FREQUENCIES (cm⁻¹) OF 3-BUTENYLSILANE-*d*₀^{a)}

Gas		Liquid				ρ	Solid				Calculated				Assign- ment ^{c), d)}
IR		IR		R			IR		R		CT ^{b)}	ST	SG'	SG	
2162	vs	2158	vs	2154	vvs	p	2171 sh vs (2158 vs 2148 vs	2181 vvs (2154 vvs 2149 sh vs			2174 A' 2174 A''	2174	2174	2174	ν_a SiH ₃ ν_a SiH ₃
								2127 vvs			2171 A'	2171	2171	2171	ν_s SiH ₃
1646	m	1641	w	1640	vvs	p	1639	m	1639	vs	1645 A'	1642	1642	1642	ν C=C
1445	w	1444	vw	1447 b	vw	dp							1434	1432	δ SiCH ₂
1429	w	1432 b	vw	1430 sh	vw		1430	w	(1432 sh w 1423 m		1430 A'	1427			ν =CH ₂
1416	w	1415	vw	1416	s	p	1416	vw	1415	w	1426 A'	1424	1422	1424	δ SiCH ₂ (CT, ST), ν =CH ₂ (SG', SG)
		1405	vw	1406 sh	w	dp?	(1403 vw 1400 sh vw	1407	s		1404 A'	1406	1405	1405	δ CCH ₂
1348	vw	1342	vvw	1345	vvw		1344	vw	1345	vw	1347 A'		1353	1351	w CCH ₂
1316 b	vw	1314	vvw	1317 sh	vw							1329			w CCH ₂
				1300 sh	s							1290			t CCH ₂
		1294	vvw	1295	vs	p	1298 b	vvw	1296	vs	1277 A''		1282	1283	t CCH ₂
		1262	vvw	1277	m	p	1281 b	vvw	1280	w	1269 A'	1255	1255	1256	δ =CH i. p.
				1193	w	p						1191			w SiCH ₂
1178 b	w	1181	vw	1184	w	p	1183	w	1181	m	1190 A'				w SiCH ₂
		1162	vw	1173	w	p									w SiCH ₂
				1145 b	vvw							1144	1154	1165	ν =C-C
												1145			w SiCH ₂
1089 sh	w	1095	vw	1087 b	vvw		1087	w	1095	vw	1104 A''			1100	t SiCH ₂ (CT), ν =C-C(SG)
											1093 A'			1092	ν =C-C(CT), t SiCH ₂ (SG)
1057	w	1053	vw	1057 b	vvw							1070	1047		t SiCH ₂
				1013	w							1008			ν C-C
992	s	991	m	992	w	dp?	1000	m	1003	vw	998 A''	997	1004	1003	t =CH ₂
							981	vw	985	m	984 A'		995	990	ν C-C
				942	vs	dp	939 sh	s	947 sh	vs	950 A''	950	949	950	δ_a SiH ₃
									943	vs	947 A'	947	948	948	δ_a SiH ₃
936	vs	922 b	vs	931	s	dp?	930	vs	937	m	925 A''	924	927	926	w =CH ₂
							917 b	vs	922	w	917 A'	917	917	917	δ_s SiH ₃
		908 sh	vs	912	m	dp?			909	w	903 A'	905	904	909	ν =CH ₂ (CT, ST, SG'), ν CCH ₂ (SG)
				898	w	p	904	vs	901	m	900 A''	896			ν CCH ₂
				878	vw								887	885	ν CCH ₂ (SG'), ν =CH ₂ (SG)
802	m	799	w	800	vw								801		ν SiCH ₂
		789 sh	w	790 sh	vvw									787	ν SiCH ₂
753	m	757 b	w	758	s	p	760	m	763	vs	763 A'	758			ν C-Si
		749 b	w	745	w	dp?	748	m	746	vvw	731 A''	728			ν SiCH ₂
				699 sh	w									696	ν C-Si
697	w	692	w	693	m	p							692		ν C-Si
				661 sh	w								628	631	δ =CH o. p.
		643	vw	651	w	dp?						623			δ =CH o. p.
		604	vw	610	w	p	601	m	(613 s 607 m		602 A'				ν_s SiH ₃
582 b	w	578	w	584	vs	p						568	569	574	ν_s SiH ₃
		549	vw	555 b	vw		552	w	554	w	563 A''				δ =CH o. p.
524 b	m	522 b	vw	525	w	dp?	528	w	(538 w 528 w		538 A'' 525 A'	539	537	537	ν_a SiH ₃ δ C=CC
				433 sh	w								440		δ C=CC
424 b	vw	422	vvw	423	m	p						439		438	δ C=CC

TABLE 1. (Continued)

Gas	Liquid		ρ	Solid		Calculated				Assign- ment ^(c),d)
IR	IR	R		IR	R	CT ^{b)}	ST	SG'	SG	
		332 sh vw						369	371	$\delta\text{CCC}=\text{C}$
		305 w p					321			$\delta\text{CCC}=\text{C}$
		261 w p		264 m		243 A'				δCCSi
		224 b w dp?						229	219	δCCSi
				208 w						106×2
		179 sh m dp?		179 w		161 A'	188			$\delta\text{CCC}=\text{(CT)},$ $\delta\text{CCSi(ST)}$
				158 w		162 A''				$\tau\text{C-Si}$
							156	140	139	$\tau\text{C-Si}$
		96 sh m dp?		106 vs		131 A''	95	91	96	$\tau=\text{C-C}$
				(92 vs 88 vs		75 A''				$\tau\text{C-C}$
							78	69	69	$\tau\text{C-C}$
				79 sh m						} Lattice vibrations
				59 s						
				52 vs						
				36 vvs						

a) Frequencies above 2200 cm^{-1} are not included, and infrared spectra below 250 cm^{-1} are not recorded. s: strong, m: medium, w: weak, v: very, sh: shoulder, b: broad, p: polarized, and dp: depolarized. b) A', A'': A' and A'' species in the C_s symmetry. c) When molecular symbols are not indicated in parentheses, the band is assigned to each of the existing forms (CT, ST, SG', and SG). ν : stretching, σ : scissoring, w : wagging, t : twisting, r : rocking, δ : deformation, i. p.: in-plane, o. p.: out-of-plane, a: asymmetric mode, and s: symmetric mode. d) A large mixing of the modes occurred. ($t\text{CCH}_2$, $t\text{SiCH}_2$), ($\nu=\text{C-C}$, $r=\text{CH}_2$), and (δCCSi , $\delta\text{CCC}=\text{C}$) for CT. ($r_s\text{SiH}_3$, $\delta=\text{CH}$ o. p.) for ST, SG', and SG. ($\delta=\text{CH}$ i. p., $w\text{SiCH}_2$, $t\text{CCH}_2$) for SG' and SG. ($\delta=\text{CH}$ o. p., $w=\text{CH}_2$, $t=\text{CH}_2$) and ($r\text{CCH}_2$, $r\text{SiCH}_2$, $w=\text{CH}_2$) for SG.

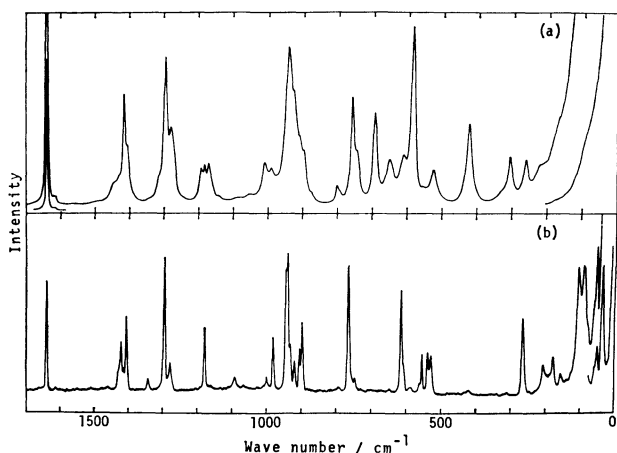


Fig. 1. Raman spectra of 3-butenylsilane- d_0 in the $10\text{--}1700\text{ cm}^{-1}$ region.

(a): Liquid state at room temperature, (b): solid state at liquid nitrogen temperature.

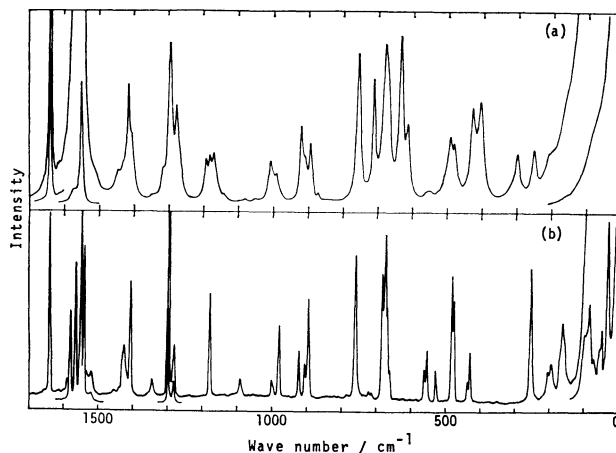


Fig. 2. Raman spectra of 3-butenylsilane- d_3 in the $10\text{--}1700\text{ cm}^{-1}$ region.

(a): Liquid state at room temperature, (b): solid state at liquid nitrogen temperature.

silane containing a $-\text{CH}_2\text{CH}_2\text{SiH}_3$ group, only the C-Si stretching and CH_2Si rocking vibrations have been observed in the $650\text{--}850\text{ cm}^{-1}$ region.¹¹⁾ By analogy with the case of the C-Cl stretching vibration in alkyl chlorides,¹⁴⁾ the C-Si stretching vibration for the T form (P_C) has been assigned on a higher-frequency side than that for the G form (P_H), while the reverse is true for the CH_2Si rocking vibration,¹⁵⁾ as is shown in Fig. 3. The CH_2Si rocking vibration, however, is, in general, weak in the Raman scattering and is of medium strength in the infrared

absorption. Thus, from a comparison of the spectra of BS- d_0 with those of propylsilane and butylsilane, the stronger Raman lines at 758, 699 (shoulder), and 693 cm^{-1} are assigned to the C-Si stretching vibration, while the Raman lines at 800, 790 (shoulder), and 745 cm^{-1} are assigned to the CH_2Si rocking vibration. The Raman lines at 800, 790, 699, and 693 cm^{-1} , vanishing in the solid state, belong to the G form, and the Raman lines at 758 and 745 cm^{-1} , persisting in the solid state, to the T form.

On the other hand, for 1-butene¹²⁾ and allyl chlo-

TABLE 2. OBSERVED AND CALCULATED FREQUENCIES (cm⁻¹) OF 3-BUTENYLSILANE-*d*₃^{a)}

Gas	Liquid						Solid				Calculated				Assign- ment ^{b), d)}
	IR	IR	R		ρ		IR	R			CT ^{b)}	ST	SG'	SG	
1646	m	1641	m	1639	vvs	p	1641	s	1640	vs	1645 A'	1642	1642	1642	ν C=C
1575	vs	1571	vs	1570	vvs	dp?	1580	vs	1589	vs	1572 A'	1572	1572	1572	ν_a SiD ₃
							1565	vs	1564	vs	1572 A''	1572	1572	1572	ν_a SiD ₃
1564	vs	1550	vs	1551	vvs	p	1552	vs	(1549 1539	vvs vvs	1545 A'	1545	1545	1545	ν_s SiD ₃
				1528 sh	w				1521	vw					755 × 2
1443	w	1445	w	1446	w	dp							1434	1432	δ SiCH ₂
1430	w	1431	w	1432 sh	w		1429	s	1425	w	1430 A'	1427			δ =CH ₂
1417	w	1415	w	1416	s	p	1418 sh	vw	1416 sh	vw	1426 A'	1424	1422	1424	δ SiCH ₂ (CT, ST), δ =CH ₂ (SG', SG)
		1407	w	1407 sh	m	dp?	(1406 m 1401 sh vw	1407	s	1404 A'	1406	1405	1405		δ CCH ₂
		1359 sh	vw												677 × 2
1356 b	vw	1345	vw	1346	vw		1343	vw	1344	vw	1347 A'		1353	1351	ω CCH ₂
1314 b	vw	1317	vw	1314	w	p						1329			ω CCH ₂
				1299 sh	s							1290			ι CCH ₂
1299 sh	vw	1295	vw	1295	vs	p	1299	vw	1296	vs	1277 A''		1282	1283	ι CCH ₂
1260	vw	1263	vw	1278	m	p	1283	vw	1280	w	1269 A'	1255	1255	1256	δ =CH i. p.
				1194	w	p						1190			ω SiCH ₂
1170 b	vw	1180	vw	1182	w	p	1180	m	1179	s	1188 A'				ω SiCH ₂
		1161	vw	1171	w	p									ω SiCH ₂
				1142 b	vw							1143	1154	1164	ν =C-C
												1144			ω SiCH ₂
1088 b	vw	1094	vw	1084	vw		1090	m	1092	vw	1103 A''			1098	ι SiCH ₂ (CT), ν =C-C(SG)
											1093 A'			1091	ν =C-C(CT), ι SiCH ₂ (SG)
1054	w	1052	vw	1053	vw							1068	1046		ι SiCH ₂
		1010	w	1007	w							1005	1003	1002	ν C-C(ST), ι =CH ₂ (SG', SG)
999	m	992	m	994	w	dp?	997	m	1002	vw	997 A''	996	993	988	ι =CH ₂ (CT, ST), ν C-C (SG', SG)
				986 sh	vw		983	w	981	m	980 A'				ν C-C
918	s	918	s	921	m	p			925	w	924 A''	923	927	925	ω =CH ₂
912	s			912	w	dp?	903	vs	907	w	903 A'	903	900	905	r =CH ₂ (CT, ST, SG'), r CCH ₂ (SG)
		901	vs	896	w	p	895 sh	m	896	m	892 A''				r CCH ₂
				871	vw							887	886	884	r CCH ₂ (ST, SG'), r =CH ₂ (SG)
760	vs	756	vs	755	vs	p	764	vs	761	s	770 A'	766	785	770	ν C-Si(CT, ST), ν SiCH ₂ (SG', SG)
716	vs	710	vs	713	s	p	(727 m 723 m 688 sh vw 674 vs 666 vs 662 vs	(722 vw 714 vw 684 s 674 vs 668 m 661 vw	718 A''	716	717	715			r SiCH ₂ (CT, ST), ν C-Si (SG', SG)
676	vs	677 b	vs	678 b	vs	dp?					681 A'' 680 A'	680 680 662	681 680 680	681 680 680	δ_a SiD ₃ δ_a SiD ₃ δ_s SiD ₃ δ_s SiD ₃
635	m	635	w	634	vs	p							638	644	δ_s SiD ₃
		610 sh	vw	614	m	p						593	608	613	δ =CH o. p.
		547 b	vw	556	vw	dp?	552	w	(562 559	vw w	563 A''				δ =CH o. p.

TABLE 2. (Continued)

Gas	Liquid			ρ	Solid			Calculated				Assign- ment ^{(9), (d)}
	IR	IR	R		IR	R		CT ^(b)	ST	SG'	SG	
			520 sh vw		521 vw	529 vw		537 A'				$\delta\text{C}=\text{CC}$
492 b w	489 b w	492 m							492	483	496	$r_s\text{SiD}_3$
	477 w	481 w			474 s	(482 s 476 m)		460 A'				$r_s\text{SiD}_3$
424 b w	437 w	428 m	p		(434 m	(438 vw 430 w			424	439	422	$r_a\text{SiD}_3$ (ST), $\delta\text{C}=\text{CC}$ (SG', SG)
		406 m	p		427 sh w			419 A''		416	418	$r_a\text{SiD}_3$
		319 sh vw							409			$\delta\text{C}=\text{CC}$
		300 vw	p							350	351	$\delta\text{CCC}=\text{C}$
		253 w	p			255 s		230 A'	316			$\delta\text{CCC}=\text{C}$
		211 w	dp?									δCCSi
						(206 vw 196 w				215	207	δCCSi
		168 sh w	dp?			165 m		154 A'	175			102×2
								149 A''	129	113	113	$\delta\text{CCC}=\text{C}$ (CT), δCCSi (ST)
		100 sh s	dp?			102 vvs		112 A''	86	80	85	$\tau\text{C}-\text{Si}$
						88 s		69 A''				$\tau\text{C}-\text{C}$
									76	66	67	$\tau\text{C}-\text{C}$
						73 s						} Lattice vibrations
						52 vs						
						35 vs						

a), b), c) See a), b), and c) of Table 1. d) A large mixing of the modes occurred. ($t\text{CCH}_2$, $t\text{SiCH}_2$), ($\nu=\text{C}-\text{C}$, $r=\text{CH}_2$), (δCCSi , $\delta\text{CCC}=\text{C}$), and ($\tau\text{C}-\text{Si}$, $\tau=\text{C}-\text{C}$) for CT. ($r_a\text{SiD}_3$, $\delta\text{C}=\text{CC}$) for ST. ($w\text{SiCH}_2$, $t\text{CCH}_2$, $\delta=\text{CH}$ i.p.) and ($\delta=\text{CH}$ o.p., $t=\text{CH}_2$, $w=\text{CH}_2$) for SG' and SG. ($r\text{CCH}_2$, $r\text{SiCH}_2$, $w=\text{CH}_2$) for SG.

ride,¹⁶⁾ both containing the $\text{CH}_2=\text{CHCH}_2-$ group, the $\text{C}=\text{CC}$ skeletal bending vibration can be expected to be in the $400\text{--}550\text{ cm}^{-1}$ region; this vibration for

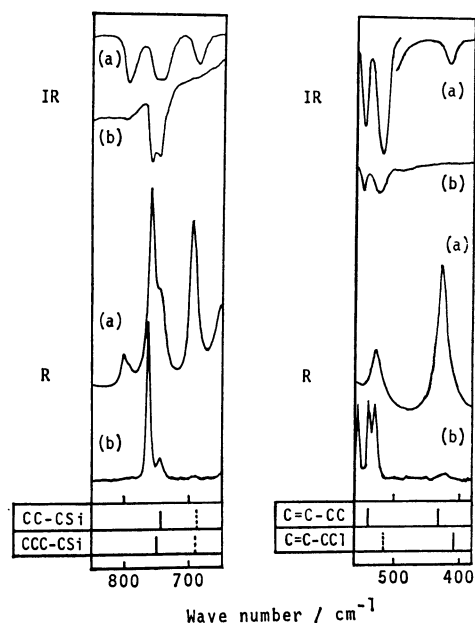


Fig. 3. Comparison of the spectra of 3-butenylsilane- d_0 with those of analogous molecules. (a): Liquid state at room temperature, (b): solid state at liquid nitrogen temperature.

the C form has been observed on a higher-frequency side than that for the S form, as is shown in Fig. 3. For BS- d_0 , the Raman lines at 525 and 423 cm^{-1} are assigned to the $\text{C}=\text{CC}$ skeletal bending vibration; the latter (the S form) disappears in the solid state, while the former (the C form) persists. Therefore, for 3-butenylsilane, it is indicated that the CT form persists in the solid state and that the CT and other forms coexist in both the gaseous and liquid states. The above results were confirmed from the normal coordinate treatment. The calculated frequencies of the CT form reproduced well the observed frequencies in the solid state. In the liquid state, the observed spectra were explained by the coexistence of the CT, ST, SG, and SG' forms. Especially, the Raman lines at 305 cm^{-1} for BS- d_0 and at 300 cm^{-1} for BS- d_3 in the liquid state suggested the existence of the ST form, corresponding to the calculated frequencies of 321 cm^{-1} for BS- d_0 and 316 cm^{-1} for BS- d_3 given in Tables 1 and 2. The Raman lines at 800 and 693 cm^{-1} and the shoulder Raman lines at 790 and 699 cm^{-1} were assigned to the vibrations of the SG' and SG forms respectively, as Fig. 4 shows. The existence of the CG form was not clear from the comparison of the observed frequencies with the calculated ones. However, this form is unlikely because of its large $\text{H}\cdots\text{H}$ nonbonded repulsion between the $\text{CH}_2=\text{CH}$ and SiH_3 or SiD_3 groups.¹²⁾

Stability of the Rotational Isomers. The enthalpy difference can be determined from the intensity ratios

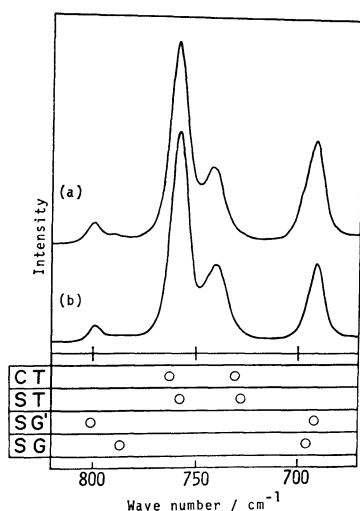


Fig. 4. Observed spectra in the 640–840 cm^{-1} region and calculated frequencies of each molecular form for 3-butenylsilane- d_0 .

(a): Liquid state at -84°C , (b): liquid state at -115°C , ○: calculated frequency.

of the Raman lines belonging to different isomers.¹⁷⁾ However, only two pairs of the Raman lines were used for the determination because of the requirement that the pair of Raman lines be well separated from each other. The relative intensities were measured in the liquid state at different temperatures between -53°C and -115°C . The intensity ratios of the Raman lines at 758 (the CT and ST forms) and 693 cm^{-1} (the SG and SG' forms) gave the apparent enthalpy difference, $\Delta H[(\text{SG} + \text{SG}') - (\text{CT} + \text{ST})] = 0.74 \pm 0.1 \text{ kcal/mol}$, and those at 261 (the CT form) and 305 cm^{-1} (the ST form), $\Delta H(\text{ST} - \text{CT}) = 0.22 \pm 0.2 \text{ kcal/mol}$. On the other hand, Fig. 4 shows that the 800 and 693 cm^{-1} Raman lines assigned to the SG' form increase in their relative intensities with a decrease in the temperature, as compared with those of the 790 and 699 cm^{-1} Raman lines assigned to the SG form. Therefore, for 3-butenylsilane, the stability of the rotational isomers is in this order: $\text{CT} \geq \text{ST} > \text{SG}' > \text{SG}$ in the liquid state.

Discussion

For 3-butenylsilane, it was found that only the CT form persisted in the solid state and that the stability of the rotational isomers was in this order: $\text{CT} \geq \text{ST} > \text{SG}' > \text{SG}$ in the liquid state. From the intensity ratios of the Raman lines belonging to the isomers, the enthalpy difference between the T and G conformations about the $(=\text{CH})\text{CH}_2\text{--CH}_2(\text{SiH}_3)$ axis was estimated to be *ca.* 0.7 kcal/mol, and that the C and S conformations about the $(\text{CH}_2=)\text{CH--CH}_2(\text{CH}_2)$ axis, $0.22 \pm 0.2 \text{ kcal/mol}$. For propylsilane with the $(\text{CH}_3)\text{CH}_2\text{--CH}_2(\text{SiH}_3)$ axis, the T form has been found from the Raman spectral analysis¹¹⁾ to be more stable than the G form by 0.60–0.65 kcal/mol. For 1-butene with the $(\text{CH}_2=)\text{CH--CH}_2(\text{CH}_3)$ axis, the enthalpy difference between the C and S forms has been reported to be $\Delta H(\text{C--S}) = 0.15 \pm 0.15 \text{ kcal/mol}$

from the microwave analysis⁹⁾ and $\Delta H(\text{C--S}) = -0.10 \pm 0.05 \text{ kcal/mol}$ from the NMR analysis.¹⁸⁾ Therefore, 3-butenylsilane has a rough additivity of the enthalpy differences.

On the other hand, Harrah and Mayo¹⁹⁾ have reported, on the basis of their infrared spectral analysis of 1-alkenes, that the isomer with the S conformation persists in the solid state. The molecular form (the CT form) of 3-butenylsilane in the solid state differs from that of 1-pentene. This is, however, not peculiar, for the enthalpy difference about the $(\text{CH}_2=)\text{CH--CH}_2(\text{CH}_2)$ axis is quite small.

For 3-butenylsilane, the most and the least stable isomers in the liquid state were the CT and SG forms respectively. Therefore, the stability of the rotational isomers is mainly interpreted in terms of the steric repulsion between the nonbonded hydrogen atoms. The SG form has a considerable $\text{H}\cdots\text{H}$ nonbonded repulsion between the $=\text{CH--}$ and CH_2Si groups. For the CT form, the silicon atom is more apart from the $\text{CH}_2=\text{CH}$ group geometrically. Thus, there is no appreciable interaction between the C=C bond and the silicon atom of the γ -position for 3-butenylsilane.

The authors wish to express their thanks to Dr. Hiroatsu Matsuura for his valuable discussion.

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