Vibrational study of rotational isomerism in dialkyldichlorosilanes Cl_2SiR_2 (R = Bu^n, Hex^n)

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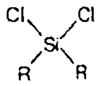
IR and Raman spectra of Cl_2SiR_2 (R = Hex^n (1), Bu^n (2)) in liquid, glassy, and polycrystalline states were investigated. In the liquid and glassy states, rotational isomerism about the Si—C and C—C bonds takes place, the compounds being mixtures of conformers. In the crystalline state, only one, the most stable conformer (all-*trans* in relation to the C—C bonds), persists. Compound 2, in contrast to 1, was found to crystallize on cooling with great difficulty.

Key words: dialkylsilanes, conformational isomerism, Raman and IR spectroscopy.

In recent years much attention has been paid to the phase transitions of poly(di-*n*-alkylsilanes), polymers that contain only silicon atoms in the backbone (see recent reviews[1,2]). In particular, the role of the conformation of the aliphatic side groups in the process of ordering of the main polymer chain has been discussed. There is a point of view (see, *e.g.*, Ref. 3) that a thermochromic phase transition, associated with transformation on cooling of the polymer backbone from a disordered to a planar zigzag all-*trans* conformation, can proceed only as a result of the side chains "crystallization" (that is, their ordering when they adopt only one, the most extended conformation). Such transformation has been observed, *e.g.*, for the most studied polysilane $[Hex^n{}_2Si]_n$ (Hex is hexyl),[3] while a phase transition of its close homologue $[Bu^n{}_2Si]_n$ proceeds quite differently. On cooling, the skeleton of the latter first transforms to a 7/3 helix, probably without ordering of the alkyl groups, and special conditions are needed to force this polymer to form a crystalline phase with the planar all-*trans* backbone conformation.[4,5]

However, as was shown recently,[6] the disordering of the side groups in the polymer $[Et_2Si]_n$ on heating to 35 °C, namely, the "defreezing" of conformational isomerism about the Si—C bonds, does not lead to the disordering of the macromolecule backbone which preserves its planar all-*trans* conformation up to 200 °C. Thus, the problem of the effect of the side group calls for further investigation.

In order to elucidate the role of the alkyl side chain conformation in polysilanes, it is necessary first to be able to distinguish between different conformations. Usually such an analysis is based on the data on vibrational spectra of various conformers of *n*-alkanes and polyethylene. However, it is evident that attachment of an alkyl group to the silicon atom will influence the symmetry and frequencies of the corresponding vibrations, at least those of adjacent CH_2 groups. That is why it seems reasonable to investigate conformational isomerism in model compounds, namely, silanes of the type Cl_2SiR_2 containing the same R as the polymer in question. The mass of the Cl atom is of the same order as that of the Si atom, so that the molecule (1) models to some extent the unit of the polymer (2).



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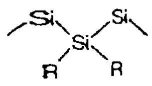

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One of the most suitable methods for the study of rotational isomerism is vibrational spectroscopy. A review[7] is specially devoted to application of Raman and IR spectroscopy to investigation of rotational isomerism in organosilicon compounds. The aim of the present work is to study rotational isomerism in two dialkyldichlorosilanes $Hex^n{}_2SiCl_2$ (1) and $Bu^n{}_2SiCl_2$ (2) by means of vibrational spectroscopy, with the view to using the results obtained for elucidating the mechanism of phase transitions of various polysilane polymers containing Bu^n and Hex^n side groups.

At room temperature, compounds 1 and 2 are liquids which should be equilibrium mixtures of various conformers. Only one, the most stable conformer, is expected to remain after crystallization on cooling.

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Experimental

The compounds studied were of commercial grade, received from the Gelest Co, Tullytown, Pennsylvania. They were purified by fractional distillation *in vacuo* just before obtaining spectra.

The Raman spectra were recorded using a U-1000 laser Raman spectrometer with excitation by the 514.5 nm line of an argon laser ILA 120-1. Samples **1** and **2**, liquids at room temperature, were sealed in glass capillaries. Depolarization ratios of the Raman lines were qualitatively estimated for liquid samples. For obtaining the Raman spectra at low temperatures, a Meric cryostat, type 91-Arpajon with nitrogen vapor blowing, was used. The temperature was maintained within ±1 °C.

Carl Zeiss M-80 and M-82 Carl spectrophotometers and a Bruker IFS 45 IR Fourier spectrometer were used to obtain IR spectra. Variable-temperature IR studies were carried out using an Air Products DE-202S vacuum cryostat. The substances were either placed in a cell with CsI windows (layer thickness 0.25 mm) or sublimed on a cold CsI or KBr target.

The sample of **1** easily crystallizes when cooled to about −50 °C. The sample of **2** glassifies under the same conditions. We did not succeed in obtaining the sample of **2** in the crystalline state even after repeated annealing.

The conditions for crystallization of **2** were found only after numerous experiments with variation of temperature regimes and sublimation details.

Results and Discussion

The fragment Cl_2SiC_2, common to both molecules studied, belongs to the symmetry point group C_{2v}. The vibrations of this fragment are situated in the region below 750 cm^{-1} and can be easily assigned on the basis of vibrational analysis of Cl_2SiMe_2 [8] and Cl_2HSiEt [9] (Table 1). It should be noted that some vibrations of the alkyl groups are situated also in this spectral region, for instance, the deformation of the aliphatic chain (an intense Raman line at 420 cm^{-1} in the spectrum of **2**). Vibrations of the alkyl groups should be governed by their own local symmetry which depends on conformation.

In molecules **1** and **2**, various conformers can exist due to hindered internal rotation about the Si—C and C—C bonds. The sensitivity of some vibrational frequencies to rotational isomerism about the Si—C bonds has been revealed on the basis of normal coordinate analysis of ethylchlorosilanes.[9—11] Vibrational analysis of different conformers of *n*-alkanes is presented in a classical work by Snyder[12] and also in the book[13] and papers.[14—16]

Di(*n*-hexyl)dichlorosilane. The Raman and IR spectra of a liquid sample of **1** at room temperature and below T_{melt} (at about −50 °C) are very complicated (see Figs. 1 and 2). They become much simpler when the substance transforms to an ordered crystal. The latter fact is evidenced by the appearance of narrow lines in the low-frequency Raman region, corresponding to crystal lattice vibrations. Comparison of the spectrum of the crystalline **1** with that of all-*trans* (*ttt*) *n*-hexane (Table 2)

Table 1. Assignment of the vibrations of the fragment Cl_2SiC_2 in the spectra of the crystalline Cl_2SiR_2 (R = Bu^n, Hex^n)

Symmetric species	Assignment	ν/cm^{-1}, Me_2SiCl_2 [8]	ν/cm^{-1}, I_{rel} (polarization in Raman spectra)	
			$Bu^n_2SiCl_2$	$Hex^n_2SiCl_2$
A_1	ν(Si—C)	690	697 vw	700 w
	ν(Si—Cl)	463	478 s (p)	489 vs (p)
	δ(CSiC)	232	255 s (p)	265 s (p)
	δ(ClSiCl)	168	206 s (p)	188 s (p)
B_1	ν(Si—C)	805	754 w	747 w
	γ(ClSiCl)	241	230 w	229 vw
A_2	τ(ClSiCl)	177	165 m (dp)	163 s (dp)
B_2	ν(Si—Cl)	530	518 w (dp)	524 w (dp)
	ρ(ClSiCl)	298	?	288 w

Note. Designation of normal vibrations is given according to Ref. 8. Assignment of the deformational modes is tentative; p, polarized band; dp, depolarized band.

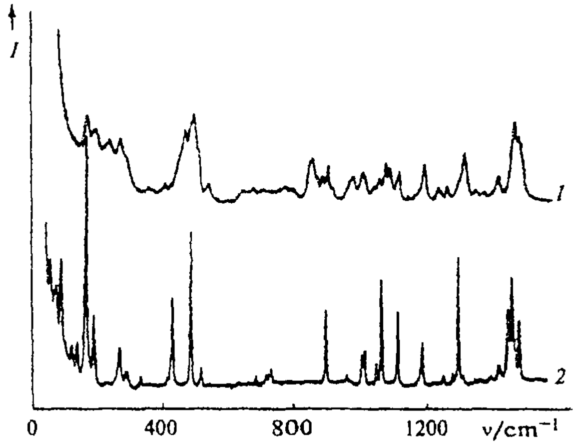

Fig. 1. Raman spectra (in the region 20—1600 cm^{-1}) of $Hex^n_2SiCl_2$ in the crystalline (*1*) and liquid (*2*) states.

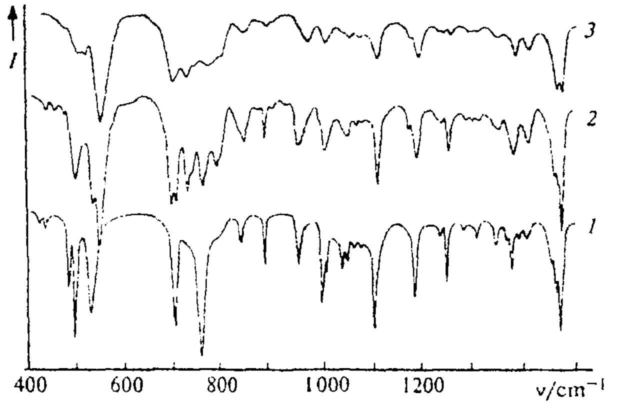

Fig. 2. IR spectra (in the region 400—1500 cm^{-1}) of $Hex^n_2SiCl_2$; *1*, crystal (−196 °C); *2*, glass (−196 °C); *3*, liquid (room temp.).

Table 2. Comparison of the vibrational frequencies of the *n*-hexyl group in the spectra of the crystalline $Hex^n{}_2SiCl_2$ and of the *ttt* conformer of *n*-hexane

ν/cm^{-1}	*ttt* *n*-hexane[12]			$Hex^n{}_2SiCl_2$ (cryst.)	
	symmetric species	activity	assignment*	activity	ν/cm^{-1}, I_{rel}
468	B_u	IR	ω, β	IR	480 m
721	A_u	IR	P	IR	727 m
798	A_u	IR	P, β	IR	757 vs
886	B_u	IR	R, β	IR	892 s
896	A_g	Raman	β, R	Raman	892 s
996	A_u	IR	T, β	IR	994 s
1010	A_g	Raman	R	Raman	1010 m
1041	B_u	IR	R, β	Raman, IR	1044 w
1060	A_g	Raman	R, W	Raman	1060 s
1143	A_g	Raman	R, β	Raman	1120 s
1242	B_u	IR	W	IR, Raman	1251 w
1302	A_g	Raman	W, R	Raman	1300 vs
1369	B_u	IR	U	IR	1352 w
1450	A_g	Raman	δ, Γ	Raman	1452 s
1462	A_g	Raman	α, δ	Raman	1471 s
1475	B_u	IR	δ, Γ	IR	1466 vs

*Vibrational coordinates are designated according to Ref. 12.

leads to an unambiguous conclusion that the *n*-hexyl tails in the polycrystalline **1** adopt a single conformation — *ttt* in relation to the C—C bonds. Indeed, both spectra are very close in number, activity, and frequencies of spectral features in the region of 800—1500 cm^{-1}. The very simple spectral pattern of the crystalline **1** in the region of stretching ν(Si—C) vibrations points to a single conformation also in relation to the Si—C bonds. However, it is impossible to elucidate this conformation from vibrational spectra alone.

The spectrum of the liquid **1** differs dramatically from that of the polycrystalline **1** in all regions. New features are observed as in the region of vibrations of the fragment Cl_2SiC_2 (in particular, in those of the skeleton deformations 160—350 cm^{-1}, ν(Si—Cl) stretches 450—550 cm^{-1}, ν(Si—C) stretches 650—750 cm^{-1}) as in the region 750—1500 cm^{-1} where the internal vibrations of *n*-hexyl groups are situated. Particularly informative are the regions of rocking and wagging vibrations of the CH_2 and CH_3 groups, 750—900 and 1300—1400 cm^{-1}, respectively. The bands in the latter region, exhibited by the spectrum of the liquid, point to the *tg*, *gt*, and *gg* conformations at the alkyl group ends.[14] It is also important to notice the appearance in the Raman spectrum of the liquid of a new line at 1080 cm^{-1}, which is usually associated with *gauche* units in the aliphatic chain, while the neighboring line at 1080 cm^{-1} is indicative of *trans* units.

From the results obtained it is evident that liquid **1** consists of different conformers due to hindered internal rotation about the Si—C as well as the C—C bonds, while only one conformer, that with the planar all-*trans* conformation of the C—C bonds in the *n*-hexyl group, persists in the crystalline state.

While studying variable-temperature IR spectra of **1**, we were able to transform the liquid sample not only to the crystalline state by slow equilibrium cooling but also to a glassy state by fast cooling. This allows one to compare the spectra of the polycrystal and the glass at one and the same low temperature and thus eliminate the temperature effects on the parameters of the spectral bands. The difference between the spectra of liquid and glassy samples is natural; it consists in a change in band widths and intensity redistribution (see Fig. 2). The latter is due to a temperature shift of the conformational eqiulibrium.

Di(*n*-butyl)dichlorosilane. This molecule possesses less conformational freedom than **1**, and one might expect that it would order itself on cooling even more easily than **1**. However, this is not the case. It was only in one experiment that we managed to obtain the spectra of the crystalline **2** (Figs. 3 and 4, curves *1*). In all the rest of the numerous experiments, in spite of all efforts and improvisations (*e.g.*, sample annealing, different temperature regimes, various targets, introduction of nucleation centers), the sample inevitably glassified on cooling. It is notable that in the studies of alkyl derivatives of other nontransition metals (Ga, Sn), the tendency of the *n*-butyl derivatives to glassification has also been observed.[17]

To assign the spectra of **2**, the data on vibrational analysis of *trans* and *gauche* conformers of *n*-butane were used.[12,15]

The Raman and IR spectra of the polycrystalline **2** are rather simple and exhibit very narrow features (see Figs. 3 and 4, curves *1*). A clear-cut phonon spectrum is observed in the low-frequency Raman region. The frequencies of the vibrations localized in the *n*-butyl groups are close to those of the *trans* conformer of *n*-butane. From the latter fact it follows that in the crystalline **2**, the *n*-butyl groups also adopt the *trans* conformation about the C—C bonds.

In the low-frequency Raman spectrum of the glassy sample **2** (see Fig. 3, curve *2*) there are no more lines of

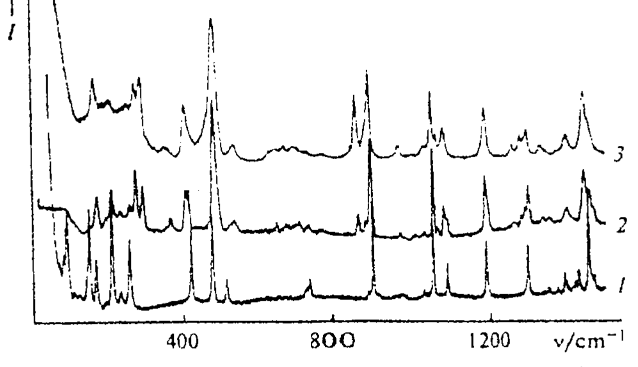

Fig. 3. Raman spectra (in the region 20—1600 cm^{-1}) of $Bu^n{}_2SiCl_2$: *1*, crystal (−180 °C); *2*, glass (−180 °C); *3*, liquid (room temp.).

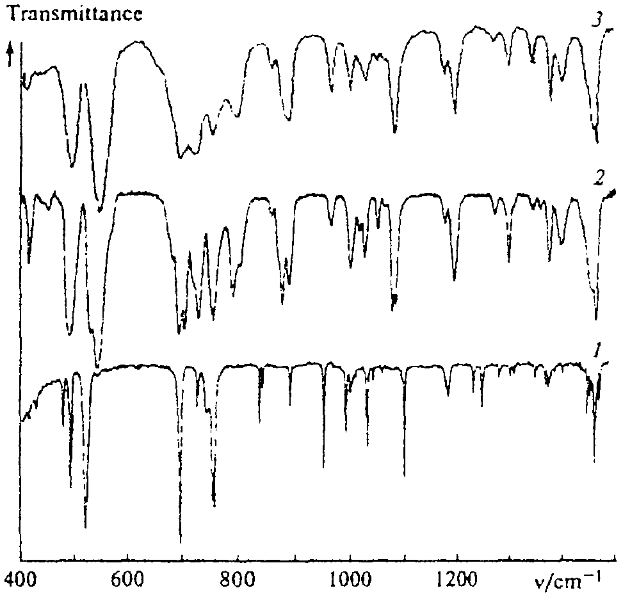

Fig. 4. IR spectra (in the region 400—1500 cm^{-1}) of $Bu^n{}_2SiCl_2$: *1*, crystal (−220 °C); *2*, glass (−220 °C); *3*, liquid (room temp.).

the phonon spectrum, but a weak broad feature appears instead, which is characteristic of the glassy state of organic compounds.[18] In all the rest of the spectral regions new lines appear. One can note the complication of the glass spectrum in the ν(Si—C) region 650—750 cm^{-1}, new lines at 368, 406, 854, 1062, 1080, 1273, 1291, 1346 cm^{-1}, and also alteration of the complex pattern near 1450 cm^{-1}. These data show that the glassy sample of **2** at low temperature is a mixture of conformers due to hindered rotation about the Si—C and C—C bonds. The frequencies of some new lines are close to those calculated for the *gauche* conformer of *n*-butane.[15]

It is interesting that the IR spectrum of the glassy sample **2** (see Fig. 4, curve *2*) exhibits a clear and reversible temperature dependence. In particular, on further cooling, the intensity of the "new" bands, which differ the spectrum of the glass from that of the polycrystalline sample, decreases. Figure 5 presents the temperature evolution of the IR region where the conformation-sensitive CH_2 wagging modes are situated. The bands at 1345 and 1357 cm^{-1} correspond to *gauche* and *trans* units about the C—C bonds, respectively. These results show that even in the glassy state molecular mobility is still sufficient to enable temperature-dependent conformational equilibrium. It is also evident from these data that the conformers which appear in the glassy sample are energetically less favorable than the conformer persisting in the crystalline state.

The Raman and IR spectra of the liquid **2** (see Figs. 3 and 4, curves *3*) are close to the spectra of the glass. The difference is only in regular band broadening and intensity increase of the "new" (compared to the

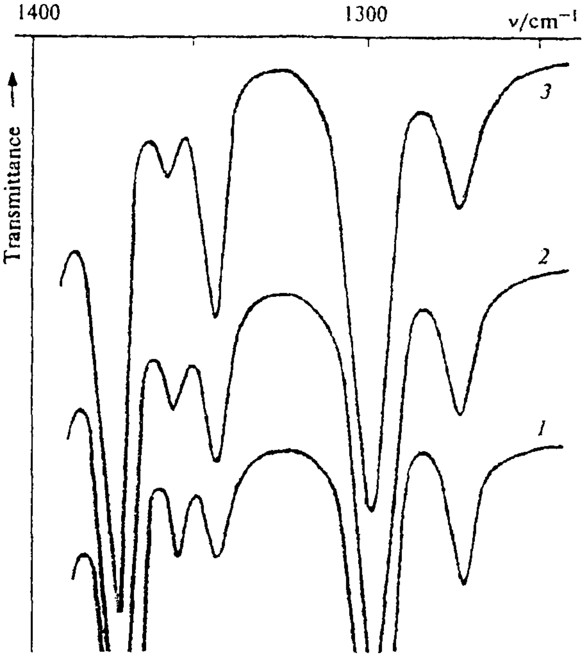

Fig. 5. Temperature evolution of the IR spectrum of the glassy $Bu^n{}_2SiCl_2$ in the region of the CH_2 wagging vibrations: −220 °C (*1*); −150 °C (*2*); −50 °C (*3*).

spectrum of the crystal) features due to the temperature shift of the conformational equilibrium towards the increase in the concentration of less stable conformers.

Thus, compounds **1** and **2** exist in the liquid and glassy states as mixtures of conformers due to hindered rotation about the Si—C and C—C bonds, while only one, the most energetically favorable conformer (all-*trans* in relation to the C—C bonds), persists in the crystalline state. In contrast to **1**, **2** crystallizes with great difficulty. As a rule, on cooling, **2** transforms to a glass. It is the difficulty of ordering of the *n*-butyl groups that seems to be the reason for the above-mentioned difference in the nature of the phase transitions of the corresponding poly(dialkylsilanes).

The results obtained enable one to elucidate the conformation of the alkyl substituents in poly(dialkylsilanes) containing *n*-butyl and *n*-hexyl groups on the basis of the Raman and IR spectra.

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